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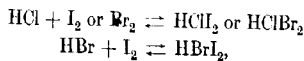
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CLXXI.—*Formation and Dissociation of some Polyhalogen Compounds of Hydrogen in Aqueous Solution.*

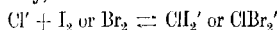
By PRIYADARANJAN RÂY and PULIN VIHARI SARKAR.

JAKOWKIN (*Z. physikal. Chem.*, 1896, **20**, 19) studied the dissociation of polyhalogen compounds of metals of the type  $XI_3$ ,  $XBr_3$ ,  $XCl_2$ ,  $XClBr_2$ , and  $XBrI_2$  (where X stands for Na, K, Li, or  $\frac{1}{2}$ Ba) as well as of  $HI_3$  in aqueous solution with the aid of the distribution method. The dissociation of  $KI_3$  and  $HI_3$  in aqueous solution at a different temperature has also been investigated by Dawson (T., 1901, **79**, 238). In the present paper, we have shown that the formation of polyhalogen compounds of hydrogen, like  $HClI_2$ ,  $HClBr_2$ , and  $HBrI_2$ , in aqueous solution can be definitely established with the aid of the distribution method, and their degree of dissociation examined. In connexion herewith, it may be mentioned that Mellor (T., 1901, **79**, 225) has also studied the formation and dissociation of  $HCl_3$  in aqueous solution with the aid of the solubility method. So the series of polyhalogen compounds of hydrogen may now be regarded as complete. Higher polyhaloids like  $HI_5$  have also been found by Jakowkin to exist to some extent in strong solutions of iodine in hydriodic acid (*loc. cit.*). The analogy between the alkali polyhaloids and the hydrogen polyhaloids is therefore complete. The only difference lies in their comparative stability; whereas some of the alkali polyhaloids, specially the caesium and rubidium compounds, have been isolated in the free state, none of the hydrogen compounds can be thus obtained.

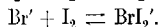
In the following experiments, the dissociation constant has been calculated according to a convenient formula employed by Jakowkin, namely,  $K = \alpha(a - 1 + \alpha)/v(1 - \alpha)$ , where  $K$  is the dissociation constant,  $\alpha$  is the degree of dissociation, which is equal to  $C/ch$ , where  $C$  is the concentration of the halogen in the carbon disulphide or carbon tetrachloride layer,  $c$  is the concentration of the halogen in the aqueous phase, and  $h$  the distribution coefficient, is the volume in litres containing 1 gram-mol. of the halogen element in the aqueous phase, and  $a$  is the gram-molecular concentration of the halogen acid in volume  $v$ . Applying the law of mass action for volume  $v$ , the above equation is obtained for the balanced reactions



or, expressed ionically,



and



The concentration of free iodine or bromine is  $\alpha/v$ , that of  $\text{HCH}_2$  is  $(1 - \alpha)/v$ , and that of  $\text{HCl}$  is  $(a - 1 + \alpha)/v$ .

In order that the equation of equilibrium may acquire the simple form given above, it is necessary to assume that the electrolytic dissociation of the hydrochloric or hydrobromic acid and of  $\text{HCH}_2$ ,  $\text{HClBr}_2$ , or  $\text{HBrI}_2$  is almost complete (which is not far from the actual condition); that the iodine or bromine molecules can combine equally well with the halogen ions (chlorine or bromine ions) and the undissociated halogen acid molecules ( $\text{HCl}$  or  $\text{HBr}$  molecules); and also that the undissociated complex polyhaloids, if present, must behave like the complex ions. In moderately concentrated solutions ( $2N$  or  $N$ ) of halogen acids, these assumptions become faulty to some extent, and in such cases the dissociation constants will be found to vary slightly from those obtained for more dilute solutions. The small changes due to the mutual solubility of the two solvents and the influence of the dissolved substance in the aqueous phase on the value of the distribution coefficient can be neglected.

#### *Formation and Dissociation of the Compound $\text{HCH}_2$ .*

The distribution of iodine between hydrochloric acid of varying concentration ( $2N$  down to  $N/16$ ) and carbon disulphide, carbon tetrachloride, or chloroform was studied. For this purpose, in the case of carbon disulphide, the hydrochloric acid (250–400 c.c.) was shaken mechanically at the ordinary temperature with iodine and the organic solvent (50 c.c.) in well-stoppered, glass bottles of 500–750 c.c. capacity until equilibrium was established. When the immiscible solvents had separated completely, the concentration of the halogen in each layer was determined, 100–300 c.c. of the aqueous layer and 5–10 c.c. of the carbon disulphide being titrated in each case, the first with  $N/100$  and the second with  $N/10$  thiosulphate. The constancy of the value of  $K$  calculated on the assumption that the compound  $\text{HCH}_2$  is formed (Table I) justifies the assumption. The values of the distribution coefficient ( $h$ ) are taken from Jakowkin's results.

The mean value of  $K$  is 0.623 with hydrochloric acid of all the preceding concentrations.

It will appear from the above table that the dissociation of the  $\text{HCH}_2$  molecules or of the complex  $\text{CH}_2$  ions increases as the concentration of the hydrochloric acid diminishes. In  $N/16$  hydrochloric acid about 90 per cent. is dissociated. We may therefore

TABLE I.

Distribution of iodine between carbon disulphide and hydrochloric acid at 25°.

c.	C.	h.	v.	a.	K.
<b>2N-HCl</b>					
0.3930	55.46	589.9	646.3	0.3392	0.64
0.4488	65.0	593.0	565.8	0.2464	0.605
			Mean 0.2428		0.622
<b>N-HCl</b>					
0.0421	9.198	582	6033	0.3754	0.604
0.0836	18.07	582.5	3040	0.3712	0.592
0.1359	28.32	583.5	1869	0.3572	0.597
0.2237	49.42	588	1135	0.3757	0.602
0.2425	55.46	589.9	1048	0.3877	0.630
0.4079	90.22	607	622.6	0.3643	0.594
0.4863	110.0	619	522.3	0.3655	0.597
0.6797	168.4	659.5	373.6	0.3755	0.595
			Mean 0.3715		0.604
<b>N/2-HCl</b>					
0.03238	10.46	582	7843	0.5551	0.622
0.05872	18.96	582.5	4326	0.5550	0.622
0.0969	29.591	583.8	2621	0.5230	0.596
0.1659	54.92	589.5	1531	0.5616	0.636
0.1898	61.86	592	1339	0.5506	0.644
0.1890	63.23	592.8	1344	0.5643	0.648
0.3222	109.0	618.5	788.1	0.5468	0.642
0.3897	131.5	634	651.8	0.5322	0.598
			Mean 0.5486		0.626
<b>N/4-HCl</b>					
0.02461	10.363	582	10320	0.7235	0.653
0.04223	17.85	582	6015	0.7263	0.659
0.06904	28.56	583.5	3680	0.7091	0.609
0.1337	56.92	591.0	1900	0.7202	0.640
0.1442	59.58	591.0	1761	0.6990	0.628
0.2348	101.59	613.0	1081	0.7058	0.648
0.2631	115.8	623.0	965.4	0.7065	0.646
			Mean 0.7129		0.640
<b>N/8-HCl</b>					
0.08532	40.72	585.5	2977	0.8151	0.627
0.1020	49.87	588.2	2490	0.8312	0.616
			Mean 0.8231		0.6215
<b>N/16-HCl</b>					
0.08362	43.49	586.5	3038	0.8867	0.612
0.09627	51.71	588.7	2638	0.9124	0.653
0.1059	56.78	591	2399	0.9074	0.610
			Mean 0.9022		0.625

conclude that the compound  $\text{HClI}_2$  or the complex  $\text{ClI}_2$  ion is incapable of independent existence in the absence of free hydrochloric acid or chlorine ions, or of iodine, the other product of its dissociation.

*Distribution of Iodine between Carbon Tetrachloride and Hydrochloric Acid at 25°.*—In this case the shaking was effected in stoppered bottles of 250–500 c.c. capacity, 100–150 c.c. of the hydrochloric acid and 50 c.c. of carbon tetrachloride solution were employed in each case, and 50–100 c.c. of the hydrochloric acid and 5–20 c.c. of the carbon tetrachloride solution were titrated with



$N/100$ - and  $N/10$ -thiosulphate respectively. The distribution coefficient was previously determined in separate experiments by shaking carbon tetrachloride and water with iodine, and the mean of the values obtained for the concentrations employed in the following determinations was taken. The mean value found was 87.

As a result of several determinations, the mean values of  $\alpha$  and  $K$  recorded in Table II were obtained at 25°.

TABLE II.

Normality of HCl.	$\alpha$ .	$K$ .
1	0.3719	0.595
0.5	0.5461	0.600
0.25	0.7176	0.635
Mean 0.610		

TABLE III.

Normality of HCl.	$\alpha$ .	$K$ .
1	0.3687	0.584
0.5	0.5480	0.606
0.25	0.7142	0.625
Mean 0.603		

*Distribution of Iodine between Chloroform and Hydrochloric Acid at 25°.*—The distribution coefficient in this case was previously determined by a number of experiments at concentrations approximately equal to those employed for the following dissociation experiments, the results of which are given in Table III. The mean value of the distribution coefficient employed was 132.

Therefore the value of the mean dissociation constant of the compound  $\text{HClI}_2$  obtained from experiments with different solvent media remains almost constant, namely, 0.623 with carbon disulphide, 0.610 with carbon tetrachloride, and 0.603 with chloroform.

*Dissociation of the Compound  $\text{HClI}_2$  determined from Solubility Measurements.*—The degree of dissociation of the compound  $\text{HClI}_2$  in hydrochloric acid of varying concentration was more conveniently investigated by means of the solubility of iodine in water and in hydrochloric acid, as shown in Table IV. The solubility of iodine in water gives the amount of free iodine, and the quantity in excess of this dissolved by hydrochloric acid gives the amount of combined iodine as  $\text{HClI}_2$  or as  $\text{CHI}_2$  ions.

TABLE IV.

Temp. 25°.

Normality of HCl.	Total solubility.	Free iodine.	Combined iodine.	$\alpha$ .	$K$ .
0	0.3454	—	—	—	—
1	0.9526	0.3454	0.6072	0.3625	0.57
0.5	0.6299	0.3454	0.2845	0.5483	0.607
0.25	0.4852	0.3454	0.1398	0.7119	0.618
0.125	0.4191	0.3454	0.0737	0.8226	0.600
0.0625	0.3810	0.3454	0.0356	0.9065	0.607
Mean 0.600					

The values of  $K$  and  $\alpha$  thus determined agree fairly well with those obtained by the distribution method.

*Formation and Dissociation of the Compound HClBr<sub>2</sub>.*

From the heat of solution of bromine in hydrochloric acid Berthelot deduced the formation of the compound HClBr<sub>2</sub> (*Compt. rend.*, 1885, **100**, 761).

The distribution of bromine between hydrochloric acid and carbon tetrachloride only was studied. Carbon disulphide could not be employed in this case on account of the tendency of bromine to act on the carbon disulphide in presence of water with the consequent formation of hydrobromic acid. This experiment and the following ones were carried out during the summer, when the room temperature was almost constant at 30°. The distribution coefficient of bromine between carbon tetrachloride and water was determined as usual and the mean of the values for the concentrations employed in the following experiments was taken.

TABLE V.

Distribution of bromine between carbon tetrachloride and hydrochloric acid at 30°.

c.	C.	h.	c.	a.	K.
N-HCl					
1.291	16.92	31	124	0.4228	0.73
1.541	19.46	"	103.9	0.4972	0.69
1.881	24.00	"	85.06	0.4115	0.70
2.989	38.38	"	53.53	0.4142	0.70
				Mean 0.4139	0.703
N/2-HCl					
0.6852	12.69	"	233.5	0.5974	0.74
0.9210	16.48	"	173.7	0.5772	0.68
2.1520	38.84	"	74.35	0.5779	0.68
				Mean 0.5842	0.70
V/4-HCl					
1.584	36.36	"	101.0	0.7403	0.71
2.246	51.87	"	71.24	0.7449	0.73
				Mean 0.7426	0.720

The mean value of *K* is 0.708 with hydrochloric acid of the preceding concentrations.

*Formation and Dissociation of the Compound HBrI<sub>2</sub>.*

The distribution coefficient of iodine between water and carbon tetrachloride was first determined at 30° for several different concentrations.

The results are tabulated below :—

c.	C.	h.	c.	C.	h.
(Aqueous layer).			(Aqueous layer).		
0.04676	3.804	81	0.09856	8.339	84.6
0.05560	4.485	81	0.1295	11.18	86.33
0.07518	6.166	82	0.2093	18.16	86.70

The distribution coefficients employed in the following determin-

ations were then obtained from a comparison of the above values, plotted on a curve.

TABLE VI.

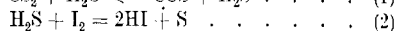
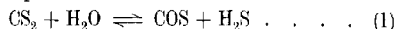
Distribution of iodine between carbon tetrachloride and hydrobromic acid at 30°.

c.	C.	h.	v.	a.	K.
N-HBr					
0.9154	4.676	81.5	277.4	0.0626	0.067
1.254	6.697	83	292.5	0.0643	0.069
1.638	8.906	84.6	155.1	0.0643	0.068
1.98	10.80	85.5	128.2	0.0638	0.068
				Mean 0.0637	0.068
N <sub>2</sub> -HBr					
0.3692	3.538	81	688	0.1183	0.067
0.6825	6.974	83	372.1	0.1231	0.070
0.8592	8.853	85	295.6	0.1212	0.069
1.007	10.42	85.5	252.3	0.1210	0.069
				Mean 0.1209	0.0687
N <sub>2</sub> /4-HBr					
0.2806	5.055	81.5	905.1	0.2210	0.071
0.4070	7.518	83	624.0	0.2225	0.071
0.4701	8.782	85	540.3	0.2197	0.070
0.6116	11.75	86.4	415.4	0.2223	0.071
				Mean 0.2214	0.07075
N <sub>2</sub> /8-HBr					
0.1451	4.296	81.5	1767	0.3632	0.071
0.2316	7.582	83	1009	0.3630	0.071
0.2844	8.782	85	893.2	0.3632	0.071
0.3855	12.07	86.4	658.8	0.3623	0.071
				Mean 0.3620	0.071

Hence the mean value of  $K$  for hydrobromic acid of the preceding concentrations = 0.0696.

*Distribution of Iodine between Carbon Disulphide and Hydrobromic Acid.*—In the following experiments the coefficients of distribution of iodine between carbon disulphide and water were calculated from Jakowkin's values for 25°, introducing necessary corrections for the rise of temperature. Dawson (*loc. cit.*) has found that for every degree rise of temperature the distribution coefficient of iodine between carbon disulphide and water increases by 0.6 per cent. The validity of this result was confirmed by carrying out a few experiments at 30°, at which temperature the following determinations were made. It should, however, be pointed out that at an elevated temperature like 30° the iodine has a tendency to act on the carbon disulphide in presence of water, especially on shaking for a long time, giving rise to hydriodic acid. This often vitiates the results unless the water is renewed after every determination. In the presence of hydrobromic acid, however, this tendency is diminished, as is shown by the almost constant value of  $K$  in the following determinations, although no special care was taken to renew the solution at the end of each experiment. This

action of iodine on carbon disulphide is best explained in the following way. At 30°, the carbon disulphide is hydrolysed to some extent on prolonged shaking with water, with the formation of hydrogen sulphide, which is then acted upon by iodine. The following scheme represents the reactions:—



A large concentration of hydrogen ion possibly hinders the first reaction.

As a result of several determinations the following mean values of  $\alpha$  and  $K$  were obtained at 30°.

TABLE VII.

*Normality of HBr.	$\alpha$ .	$K$ .
1	0.0621	0.0657
0.5	0.1214	0.069
0.25	0.2187	0.0697
0.125	0.3647	0.071

The mean value of  $K$  for all concentrations of hydrobromic acid = 0.069.

It is interesting to compare the mean values of  $K$  for  $\text{HClI}_2$ ,  $\text{HClBr}_2$ , and  $\text{HBrI}_2$  with one another and with those of  $\text{NaClI}_2$ ,  $\text{KClBr}_2$ , and  $\text{KBrI}_2$  found by Jakowkin.

	$\text{HClI}_2$ .	$\text{HClBr}_2$ .	$\text{HBrI}_2$ .	$\text{NaClI}_2$ .	$\text{KClBr}_2$ .	$\text{KBrI}_2$ .
$K$	0.60—0.62	0.71	0.069—0.070	0.44	0.73	0.078
Temp.	25°	30°	30°	25°	25°	25°

From an examination of the above values it appears that of the three polyhaloids  $\text{HClI}_2$ ,  $\text{HClBr}_2$ , and  $\text{HBrI}_2$ , the last is least dissociated and hence the most stable. This is in agreement with the general observation that weak ions exhibit the greatest tendency to combine with neutral molecules to form stable complexes. Here the bromine ion is less electronegative than the chlorine ion, hence it will combine with iodine molecules to form a complex more stable than that formed by the chlorine ion with iodine or bromine molecules. Again, on comparing the dissociation of these polyhalogeno-acids with that of the corresponding sodium or potassium salts, we find that  $\text{HClI}_2$  dissociates to a greater extent than  $\text{NaClI}_2$ , whereas  $\text{HClBr}_2$  and  $\text{HBrI}_2$  appear to be dissociated more or less to the same extent as  $\text{KClBr}_2$  and  $\text{KBrI}_2$  respectively.

We take advantage of this opportunity to express our best thanks to Professor Sir P. C. Ray for the kind interest he has taken in the present work.

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COLLEGE OF SCIENCE, CALCUTTA. [Received, January 18th, 1922.]

CLXXII.—*Physical Chemistry of the Oxides of Lead.*  
*Part IV. Red Lead and Lead Sesquioxide.*

By SAMUEL GLASSTONE.

THE object of this work was to determine by electrochemical methods the affinity relationships existing between triplumbic tetroxide (red lead) and lead monoxide and dioxide, and between lead sesquioxide and the simpler oxides. Incidentally it was hoped that light would be thrown on the question of the constitution of these more complex oxides. If the electrodes  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right.$ ,  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right.$ ,  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \\ \text{PbO} \end{smallmatrix} \right.$ , and  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \\ \text{PbO}_2 \end{smallmatrix} \right.$  are thermodynamically reversible, it should be possible to calculate the free energy relationships required from determinations of their potential. Only those involving lead dioxide, however, were found to be reversible, and so the free energy of reactions involving the monoxide was calculated indirectly by utilising the potential of the  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \right.$  electrode. From these and other measurements, it has been shown that both red lead and lead sesquioxide are definitely plumbous salts, giving  $\text{Pb}^{++}$  ions in solution.

EXPERIMENTAL.

*Red Lead.*

In setting up the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right.$  and  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right.$  electrodes, it was necessary to have each pair of oxides quite free from the third oxide, and therefore special methods were adopted for the preparation of the mixtures to ensure this being the case.

*The  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right.$  Electrode.*—Reddish-brown lead monoxide was heated with potassium nitrate so as to cause partial oxidation to red lead. The mass was cooled, extracted with water, washed, and dried. Some of this mixture was placed in an electrode-vessel, which was then filled with *N*-sodium hydroxide (free from carbonate), and a smooth platinum electrode inserted to the exclusion of air. As in previous measurements (see Part II, T., 1921, 119, 1914), the *P.D.* of the half-clement was measured against that of the standard  $\text{Hg}|\text{HgO}$  *N*- $\text{NaOH}$  electrode, using the same solution of alkali throughout. The vessels were gently shaken, and their *P.D.*s measured from day to day as described in the communication cited.

In another set of experiments, a good commercial specimen of red lead was digested with 20 per cent. alkali until free from admixed monoxide. This product was then mixed with reddish-brown, red, and yellow lead monoxide, respectively, and the potentials in *N*-sodium hydroxide measured.

In no case did the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right| \text{N-NaOH}$  electrode give any definite potential values. The results were very erratic, and altered considerably from day to day and even during measurement. It was clear that the electrode was not behaving reversibly. Lead monoxide in alkaline solution is known to give  $\text{Pb}^{++}$  and  $\text{HPbO}_2^-$  ions, and these would act reversibly with  $\text{Pb}^{++++}$  and plumbate ions respectively. Later work has shown that the plumbic-plumbous potential can be quite definite in alkaline solution, but the plumbate-plumbite electrode is somewhat unstable. It appears that in the system red lead, lead monoxide, and alkali, there are certainly no plumbic ions, although plumbate ions are possible.

*The  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right|$  Electrode.*—The mixture of red lead and lead dioxide was obtained by warming a good specimen of red lead (completely soluble in hydrochloric acid) with dilute acetic acid, which dissolved all the excess of lead monoxide and partly decomposed the red lead. Dilute nitric acid was then added to decompose about half the red lead present. The mixture was washed, dried, and made up into alkaline half-elements by the method described above. Measurements were made from day to day, the vessels being gently shaken in the meantime.

Scale  $\text{H}_2/\text{N-H} = 0$ . Measurements at room temperature ( $17^\circ$ ).

Time after setting up (in days).	0	7	14	21	Final.
<i>P.D.</i> { 1.	0.328	0.326	0.326	0.325	0.325
{ 2.	0.314	0.326	0.325	0.325	0.325
				Mean	0.325 volt.

Subsequent determinations made with red lead freed from monoxide by alkali, and with stable electrolytic lead dioxide, gave results identical with the above.

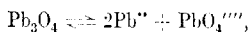
The fact that the electrode  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right| \text{N-NaOH}$  gives a definite and reproducible potential, suggests that, since lead dioxide in solution very probably gives plumbic ions, red lead in alkaline solution gives plumbous ions; and is thus a plumbous salt. The plumbous salt of the theoretical tetrabasic orthoplumbic acid,  $\text{b(OH)}_4$ , would be  $\text{Pb}_3^{++}\text{PbO}_4$ , that is,  $\text{Pb}_3\text{O}_4$ , and hence red lead probably plumbous orthoplumbate. This constitution has been

previously suggested to account for the formula and some of the chemical properties of red lead, but there has hitherto been no direct evidence that red lead is a plumbous salt giving  $\text{Pb}^{++}$  ions in solution.

Confirmation of this view was obtained by measurement of the potential of the electrode  $\text{Pb}|\text{Pb}_3\text{O}_4$  in  $N\text{-NaOH}$ , which should behave as a reversible lead electrode in contact with a solution containing a small but definite concentration of plumbous ions. The lead electrode was prepared as described in Part II of this series (*loc. cit.*), and the oxide used was washed as free as possible from monoxide by means of 20 per cent. alkali. After three days, a constant value of  $-0.610$  volt was obtained at room temperature.

Utilising the value, obtained in some work to be published later, for the  $\text{Pt} \begin{vmatrix} \text{PbO} \\ \text{PbO}_2 \end{vmatrix} N\text{-NaOH}$  potential, namely,  $0.268$  volt, and that of the  $\text{Pt} \begin{vmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{vmatrix}$  electrode,  $0.325$  volt, we see that red lead in  $N\text{-sodium hydroxide}$  gives one hundredth part of the plumbous ions given by lead monoxide in the same solvent. The latter value has already been determined in previous work as  $2.2 \times 10^{-15}$  gram-ions per litre at the ordinary temperature, hence red lead in  $N\text{-sodium hydroxide}$  gives a plumbous ion concentration of  $2.2 \times 10^{-17}$ . With this concentration the theoretical potential of the  $\text{Pb}|\text{Pb}_3\text{O}_4$   $N\text{-NaOH}$  electrode should be  $-0.617$  volt; the actual value ( $-0.610$  volt) is slightly higher, probably on account of the presence of traces of lead monoxide.

*Solubility of Red Lead.*—If we assume that all the red lead in solution has ionised thus :



then the solubility of red lead in  $N\text{-sodium hydroxide}$  is  $1.1 \times 10^{-17}$  gram-mol. per litre at  $17^\circ$ . The solubility in pure water is probably of the same order.

The solubility product of red lead,  $[\text{Pb}^{++}][\text{PbO}_4^{'''}]$ , is equal to  $(2.2 \times 10^{-17})^2 \times 1.1 \times 10^{-17}$ , that is,  $5.32 \times 10^{-31}$ .

*Dissociation Pressures.*—Red lead decomposes into lead monoxide and oxygen, but since the electrode  $\text{Pt} \begin{vmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{vmatrix}$  is not thermodynamically reversible, the dissociation pressures can only be calculated indirectly from a knowledge of the potentials of the half-elements  $\text{Pt} \begin{vmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{vmatrix}$ , and  $\text{Pt} \begin{vmatrix} \text{PbO} \\ \text{PbO}_2 \end{vmatrix}$  in  $N\text{-sodium hydroxide}$ .

The cell  $\text{Pt} \begin{vmatrix} \text{PbO} \\ \text{PbO}_2 \end{vmatrix} N\text{-NaOH } \text{H}_2(1 \text{ atm.})|\text{Pt}$  has an *E.M.F.* of

0.268—(−0.810), that is, 1.078 volts at 17°, and the reaction involved is



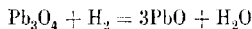
The free energy of this reaction is therefore  $1.078 \times 96540 \times 2$  joules.

The cell  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right| \text{N-NaOH } \text{H}_2(1 \text{ atm.}) | \text{Pt}$  has an *E.M.F.* of 0.325—(−0.810), that is, 1.135 volts at 17°, and the reaction involved is



the free energy of which is therefore  $1.135 \times 96540 \times 4$  joules.

From these two equations we deduce the free energy of the reaction :



as  $1.928 \times 96540$  joules. This would be the reaction occurring in the cell  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right| \text{N-NaOH } \text{H}_2(1 \text{ atm.}) | \text{Pt}$ , were it thermodynamically reversible, and its *E.M.F.* would thus be 0.964 volt. This cell may be regarded as an  $\text{H}_2\text{—O}_2$  cell in which the oxygen is supplied at the dissociation pressure of red lead, and the hydrogen at 1 atmosphere. Using the value 1.232 volts as the *E.M.F.* of the cell with both gases at 1 atmosphere, the dissociation pressure of red lead at 17° is calculated as  $3.3 \times 10^{-19}$  atm.

Reinders and Hamburger (*Z. anorg. Chem.*, 1914, **89**, 71) measured the dissociation pressure of red lead from 445° to 607°, and expressed their results in the form of the equation,  $\log p = -\frac{32406}{4.571T} + 1.75 \log T + 0.000216T + 2.8$ . Substituting the value 290° abs. for  $T$ , the corresponding value of the dissociation pressure is found to be  $6.6 \times 10^{-19}$  atm.

In order to calculate the temperature at which the oxygen dissociation pressure of red lead becomes equal to that of oxygen in the atmosphere, it is necessary to know the heat of the reaction involved. There appear to be no direct thermochemical measurements of this quantity, and therefore a mean value of 36,000 calories will be adopted from the indirect determinations of Reinders and Hamburger (*loc. cit.*), that is,  $6\text{PbO} + \text{O}_2 = 2\text{Pb}_3\text{O}_4 + 36,000 \text{ cal.}$

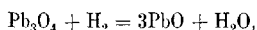
*Method 1.*—At the temperature at which the cells  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{Pb}_3\text{O}_4 \end{smallmatrix} \right| \text{N-NaOH } \text{H}_2(1 \text{ atm.}) | \text{Pt}$ , and  $\text{H}_2(1 \text{ atm.})\text{—O}_2(0.21 \text{ atm.})$  have the same *E.M.F.*, red lead will have a dissociation pressure of 0.21 atm. The *E.M.F.* of both these cells is known at 17°, and their temperature coefficients may be calculated by applying the Gibbs-



Helmholtz equation to the known heats of the reactions involved. The temperature coefficient of the first cell is  $-0.00044$ , and of the second  $-0.00090$  volt per degree. Assuming that these coefficients remain constant over several hundred degrees, we find that the *E.M.F.*'s of the two cells become equal at  $573^{\circ}$ .

*Method 2.*—By the use of the integrated form of the van't Hoff isochore, where partial pressures are involved, the temperature at which the dissociation pressure of oxygen in the reaction under consideration becomes equal to  $0.21$  atm. may be calculated as  $843^{\circ}$  abs. ( $570^{\circ}$  C.). From actual measurements of the dissociation pressure, Reinders and Hamburger (*loc. cit.*) find that red lead will decompose completely if heated in air at  $539^{\circ}$  C.

*Calculation of E.M.F. by means of Nernst's Theorem.*—By means of the Nernst theorem it is possible to calculate the *E.M.F.* of the cell  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO} \end{smallmatrix} \right| \text{H}_2(1 \text{ atm.})$  at  $0^{\circ}$ . The reaction involved is



the water being in the form of ice. For this reaction at  $17^{\circ}$ , we have:  $Q_T = 68,400$  (H, O)  $+ 1580$  (ice, water)  $- 16,750$  ( $3\text{PbO} \leftarrow \frac{1}{2}\text{O}_2 \rightarrow \text{Pb}_3\text{O}_4$ )  $= 53,230$  cals. In order to calculate the heat of this reaction at  $0^{\circ}$  abs., it is necessary to know the molecular heats of the substances involved in the reaction. In the case of red lead, no figures could be found in the literature, so the molecular heat was calculated from the variation of the heat of the reaction,  $6\text{PbO} + \text{O}_2 = 2\text{Pb}_3\text{O}_4$ , calculated by Reinders and Hamburger. Taking the molecular heat of lead monoxide as  $11.8$ , and that of oxygen as  $11.5$ , the molecular heat of red lead is found to be  $39.3$ . Using this value and the usual values of  $6.8$  for hydrogen,  $9.5$  for ice, and  $11.8$  for lead monoxide,  $Q_0$  is evaluated as  $52,550$  calories, whilst  $\beta$  is  $-0.004$ . Taking the "chemical constant" of hydrogen as  $1.6$ , the *E.M.F.* of the cell under consideration is  $0.987$  volt at  $0^{\circ}$ . Using the more approximate method in which water is involved instead of ice,  $Q_T$  becomes  $51,650$ ,  $\beta$  is  $-0.018$ , and  $Q_0$  is  $52,146$  calories. The *E.M.F.* of the cell is thus  $1.00$  volt at  $17^{\circ}$ . The actual value of the *E.M.F.* as calculated on page 1459, from measurements of the  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \right|$  and  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right|$  electrodes, is  $0.904$  volt at  $17^{\circ}$ .

*Free Energy Relations.*—By taking the free energy of the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}$  as  $1.232 \times 2 \times 96540$  joules, the free energy of the reaction  $3\text{PbO} + \frac{1}{2}\text{O}_2 = \text{Pb}_3\text{O}_4$  is  $0.536 \times 96540$  joules, that is,  $12,350$  calories at  $17^{\circ}$ . The total energy of this reaction at the same temperature is  $16,750$  calories.

*Lead Sesquioxide.*

There has been a tendency on the part of previous workers to distinguish between anhydrous lead sesquioxide,  $\text{Pb}_2\text{O}_3$ , and the hydrated form,  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . Marino (*Z. anorg. Chem.*, 1909, **62**, 173) stated that the product obtained by the action of sodium hypochlorite on a solution of lead monoxide in alkali (Winkelblech, *Annalen*, 1837, **21**, 21; Haussmann, *ibid.*, 1854, **91**, 235) is an anhydrous sesquioxide,  $\text{Pb}_2\text{O}_3$ , with basic functions. The orange-yellow precipitate obtained by mixing solutions of alkaline plumbite and plumbate (Frémy, *Ann. Chim. Phys.*, 1844, [iii], **12**, 488; Seidel, *J. pr. Chem.*, 1879, [ii], **20**, 200; Bellucci and Parravano, *Z. anorg. Chem.*, 1906, **50**, 107) was said to be the hydrated form of the sesquioxide. The latter authors suggested, from the formula and method of preparation, that the substance is plumbous meta-plumbate,  $\text{Pb}^{IV} \cdot \text{Pb}(\text{OH})_6$ .

In this work the hypochlorite and plumbite-plumbate methods were investigated in detail, but in no case could an anhydrous sesquioxide be obtained. All the products were hydrated lead sesquioxide mixed with more or less hydrated monoxide, and sometimes dioxide.

*The Hypochlorite Method.*—Reinders and Hamburger (*loc. cit.*) attempted to prepare lead sesquioxide by Winkelblech's method (*loc. cit.*) in order to investigate its oxygen dissociation pressure at various temperatures. These authors found that by varying the amount of sodium hypochlorite used, substances of formula  $\text{PbO}_x$  were obtained, where  $x$  varied from 1.41 to 1.71 ( $\text{Pb}_2\text{O}_3$  requires  $x = 1.5$ ). They inferred that the true sesquioxide does not exist and that all the products are simply solid solutions of monoxide and dioxide. Preliminary experiments by the present author confirmed the results of Reinders and Hamburger in a general way, but there appeared to be definite evidence of the existence of hydrated lead sesquioxide in the hypochlorite product. Varying amounts of sodium hypochlorite solution and sodium plumbite solution were mixed, and the products analysed by the following method. The well-washed solid was boiled for a few minutes with dilute acetic acid in order to decompose it completely. The monoxide portion dissolved in the acid, while the dioxide remained; the latter was well washed and then estimated iodometrically by the method previously described (T., 1921, **119**, 1997). The monoxide in the filtrate and washings was completely oxidised to dioxide by boiling with bromine water and a slight excess of alkali, and estimated in the usual way. By this means the ratio of  $\text{PbO} : \text{PbO}_2$  was found. To complete the analysis, the original product, having been dried to constant weight in a desiccator, was heated at a temperature sufficient to

fuse the monoxide formed, and the percentage loss was determined. Although the products obtained varied considerably and could not be duplicated, yet as long as there was no excess of lead dioxide, all the products were mixtures, or solid solutions, of hydrated sesquioxide,  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , and monoxide,  $\text{PbO} \cdot \frac{1}{2}\text{H}_2\text{O}$ . Any constitution based on the assumption that the products were simply solid solutions of monoxide and dioxide would mean that at least 7 per cent. of adsorbed water was present even after drying to constant weight over sulphuric acid. A typical analysis is the following: the  $\text{PbO}_2$ - and  $\text{PbO}$ -portions required, respectively, 5.75 c.c. and 11.55 c.c. of the same thiosulphate solution. Loss on heating = 11.7 per cent. The loss on heating a mixture of 5.75 gram-mols. of  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and 5.80 gram-mols. of  $\text{PbO} \cdot \frac{1}{2}\text{H}_2\text{O}$  would be 10.6 per cent. The difference between 11.7 and 10.6 might easily be due to adsorbed water, since the product was amorphous.

In view of the fact that a definite sesquioxide (mixed with hydrated monoxide) could be obtained by the hypochlorite method the investigation was continued. It was thought that the use of sodium hypobromite made up from known amounts of bromine and alkali, instead of hypochlorite, might give the exact conditions under which the pure hydrated sesquioxide could be obtained. The result of these experiments, summarised below, was to show that it was very improbable that this method would yield a pure product.

*Sodium Hypobromite Method.*—When sodium hypobromite (or hypochlorite) is added to an alkaline solution of lead monoxide, after one or two minutes a yellow precipitate will slowly form, which will gradually increase in amount and darken in colour. The first precipitate invariably contains excess of lead monoxide, even when, as in one case, twenty times the theoretical amount of hypobromite was used. In this case, the product obtained within the first five minutes contained 1 gram-molecule of dioxide to approximately 2 gram-molecules of monoxide; very similar results were obtained using twenty times the theoretical amount of hypochlorite. On standing, the ratio of dioxide to monoxide in the precipitate gradually increased, and the final value depended on the dilution of the mixture, the amount of alkali present, and the excess (if any) of hypobromite solution. The theoretical amount of hypobromite having been used, the composition of the precipitate, after standing for twenty-four hours, corresponded with 1 gram-molecule of monoxide to 0.7 of the dioxide; with three times the theoretical amount, the ratio of monoxide to dioxide was 1:1.2. When a fairly large excess of hypobromite had been used, the composition ultimately approached

that of lead dioxide. In one case a product of composition corresponding with the formula  $\text{Pb}_2\text{O}_3$  was obtained, but this result was purely fortuitous, as was shown by the failure to repeat it. The hypochlorite and hypobromite methods must therefore be regarded as unsatisfactory.

*The Plumbite-Plumbate Method.*—This method was also found to be untrustworthy, and certain phenomena observed in the hypochlorite and hypobromite methods were also noted in this method. It will be shown later that all these methods probably involve the same ultimate chemical reaction, consequently it is to be expected that similar results will be obtained in every case.

A solution of sodium plumbate in 10 per cent. alkali was prepared by Bellucci and Parravano's method (*loc. cit.*) for the potassium salt. This was mixed with a solution of lead monoxide in 15 per cent. sodium hydroxide. There was no immediate precipitation, but after a few minutes a yellow precipitate formed, which increased in amount and became orange on standing. The composition of this precipitate depended on the concentration of the solutions and the time of standing. When a small excess of plumbate and a large amount of alkali were used, the composition of the product approached that of lead sesquioxide, but in most cases the products were mixtures (or solid solutions) of hydrated sesquioxide and monoxide. In this and the other methods, the precipitate was sometimes deposited on the sides of the glass vessel in the form of a thin, shining, iridescent film.

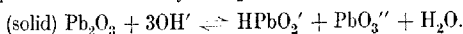
*New Method.*—The method found to be satisfactory for the preparation of fairly pure hydrated lead sesquioxide depended on the fact, which does not appear to have been previously noted, that the sesquioxide is appreciably soluble in alkali solution. Lead monoxide, however, is much more soluble, and the dioxide is almost insoluble; hence, by repeated solution in alkali and partial precipitation by acid, fairly pure hydrated sesquioxide may be obtained.

Sodium hydroxide solution (250 c.c. of 12 per cent.) saturated with lead monoxide was diluted to 500 c.c., and 500 c.c. of saturated bromine water were added. The mixture was kept over-night and then washed by decantation with water containing a little acetic acid to remove the excess of hypobromite and alkali. A paste of the precipitate and water was stirred into a solution of 60 grams of sodium hydroxide in 300 c.c. of water, warmed at  $50^\circ$ . The liquid was filtered, 40 grams of acetic acid diluted with 150 c.c. of water were slowly added to the cold filtrate with continual stirring, and the gelatinous, yellowish-brown precipitate obtained was washed by decantation and filtered, by the aid of the pump. Before drying, a small portion of the precipitate was analysed in order to determine

the ratio of dioxide to monoxide. If the precipitate still contained excess of monoxide, it was redissolved in alkali and again precipitated with acid. On drying in a desiccator, the sesquioxide darkened in colour and shrunk into small lumps, which gave a brown powder by gentle grinding; with fine grinding the colour became somewhat lighter. A product obtained by this method gave, on analysis, the ratio  $\text{PbO} : \text{PbO}_2$ , and the loss of weight on heating was 14.5 per cent.; pure  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  requires loss on heating = 13.56 per cent.

*Solubility of Lead Sesquioxide in Sodium Hydroxide Solution.*—

If a solution of lead sesquioxide in sodium hydroxide is boiled, then, provided that there is not too large an excess of alkali, lead dioxide will be precipitated and the resulting solution will contain sodium plumbite (lead monoxide). This suggests that the solution of sesquioxide in alkali contains alkaline plumbite and plumbate, for on boiling such a mixture, exactly similar results are obtained, either before or after separation of lead sesquioxide. The dissolution of sesquioxide in alkali may be represented thus :



In order to avoid complications in this and subsequent equations, the  $3\text{H}_2\text{O}$  has been omitted from the formulæ of both the sesquioxide and the plumbate ion,  $\text{Pb}(\text{OH})_6''$ ; nevertheless, the hydrated formulæ must be understood throughout.

We thus have :  $\frac{[\text{HPbO}_2'][\text{PbO}_3'']}{[\text{OH}']^3} = \text{a constant}.$

This explains all the methods of preparation of lead sesquioxide. If the solutions of plumbite and plumbate are mixed, the equilibrium constant may be exceeded, and therefore sesquioxide will be deposited. In the hypobromite and hypochlorite methods the first action is probably the oxidation of plumbite to plumbate, the next being the precipitation of the sesquioxide owing to the tendency of the equilibrium under discussion to establish itself. The reprecipitation from alkaline solution by means of acid is of course due to reduction of the hydroxyl-ion concentration. If in any method of preparation, after the removal of the precipitate, either (a) plumbite, (b) plumbate, or (c) water is added, a further precipitate will form after a few minutes; these facts are in agreement with the plumbate-plumbite-hydroxyl-ion equilibrium.

An attempt was made to verify the equilibrium equation by determining the solubility of the sesquioxide in alkaline solutions of varying concentration. With sodium hydroxide solutions of reasonable concentration, the rate of dissolution was extremely slow at the ordinary temperature, and on warming hydrolysis took place. This method was therefore abandoned. More satisfactory results were obtained by mixing solutions of plumbite, plumbate,

and dilute alkali or water in various proportions and keeping these mixtures for four or five weeks at room temperature so as to precipitate the sesquioxide. A quantity of the clear liquor was then withdrawn and titrated with standard acid. Another portion was decomposed by boiling with a slight excess of dilute acetic acid; the lead dioxide thus precipitated corresponded with the amount of plumbate present. The filtrate was oxidised by boiling alkaline hypobromite in the usual way, and the dioxide thus obtained was equivalent to the plumbite in solution.

Concentrations in gram-mols. per litre.

Sodium hydroxide.	Plumbite $\times 10^3$ .	Plumbate $\times 10^3$ .	$\frac{[\text{HPbO}_2][\text{PbO}_3'']}{[\text{OH}]^3} \times 10^6$ .
2.63	21.5	2.65	3.12
2.41	20.0	1.20	1.72
1.79	1.60	11.50	3.20
1.26	12.12	0.35	2.08
1.20	8.75	0.412	2.09

The  $[\text{HPbO}_2]$ ,  $[\text{PbO}_3'']$ , and  $[\text{OH}']$  concentrations are taken as being equal to the total amounts of plumbite, plumbate, and sodium hydroxide, respectively, without allowing for ionisation. For this reason and because the solid phase contained adsorbed hydrated monoxide (although the solutions were not nearly saturated with the latter), the results are only approximate, but on the whole they confirm the view that has been put forward regarding the equilibrium in mixtures of plumbate and plumbite solutions.

*The Plumbate-Plumbite Potential.*—According to the view put forward in the previous section, during the preparation of lead sesquioxide plumbite is oxidised to plumbate; this may be effected by chlorine, bromine, iodine, hydrogen peroxide, or potassium persulphate. Sodium plumbate, on the other hand, may be reduced to plumbite by means of nascent hydrogen (from zinc dust or aluminium powder), sodium stannite, or sodium sulphite. This reversible oxidation and reduction suggested that there might be a definite plumbate-plumbite oxidation potential, according to the equation:



The potential of an unattacked electrode (for example, platinum) placed in a solution containing plumbate, plumbite, and hydroxyl ions, would then be given by

$$E = E_0 + \frac{RT}{2F} \log \frac{[\text{PbO}_3'']}{[\text{HPbO}_2'][\text{OH}]^3}$$

where  $E_0$  is the normal oxidation-reduction potential.

Mixtures of plumbate and plumbite in sodium hydroxide solution

were kept for two or three days in order that most of the solid sesquioxide might separate, without equilibrium having been attained. Some of the clear liquid was poured into an electrode vessel, and a smooth platinum electrode inserted. After ten minutes, the potential of this electrode was measured against that of a standard alkaline electrode, saturated potassium chloride being used as intermediate liquid. Other portions of the liquid were analysed for hydroxide, plumbite, and plumbate, by the method described on page 1465. The potential of the half-element rose fairly rapidly during the first ten minutes, and then continued to rise much more slowly; owing, possibly to spontaneous changes going on in the liquid, there appeared to be no definite stable potential. By standardising the method as much as possible, results were obtained which indicated the existence of a definite plumbate-plumbite potential.

Hydrogen scale. Temperature  $17^{\circ}$  (approx.).

$\frac{[\text{PbO}_2']}{[\text{HPhO}_2]} = x$ .	Normality of NaOH.	a.	$[\text{OH}]^3 = y$ .	$\frac{x}{y}$ .	E.	$E_0$ (volt).
5.54	1.73	0.658	1.48	3.74	0.314	0.298
1.47	3.60	0.415	3.31	0.445	0.278	0.288
1.47	2.11	0.585	1.85	0.795	0.292	0.295
1.22	1.54	0.687	1.19	1.025	0.304	0.304
1.19	2.06	0.590	1.80	0.661	0.290	0.295
0.212	2.72	0.505	2.58	0.0823	0.287	0.318
0.138	2.55	0.545	2.70	0.0513	0.260	0.297

In the above calculations, the ratio of the degree of ionisation of plumbate and plumbite is assumed to be equal to unity, and  $x$ , the degree of ionisation of sodium hydroxide, has been calculated from conductivity measurements. The quantity,  $[\text{OH}]^3$ , in the above table is obtained by multiplying the amount in the second column by  $x$  and cubing the product.

The value of the normal plumbate-plumbite potential is thus of the order 0.30 volt at room temperature.

*Electromotive Behaviour of Lead Sesquioxide.*—Attempts were made to measure the potentials of the electrodes  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO} \end{smallmatrix} \right.$ ,  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{Pb}_3\text{O}_4 \end{smallmatrix} \right.$ , and  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO}_2 \end{smallmatrix} \right.$  in  $N$ -sodium hydroxide. The first two electrodes were found to be irreversible; the results were erratic, varied from day to day, and were different for different electrodes. In the case of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO} \end{smallmatrix} \right.$  electrode, the colour of the mixture changed owing to the formation of red lead.

*The  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO}_2 \end{smallmatrix} \right.$  Electrode.*—In order to obtain these two

oxides free from the monoxide, various specimens of lead sesquioxide were warmed with small amounts of dilute nitric acid in order to cause partial decomposition. The products were well washed with water and with *N*-sodium hydroxide, and made up into electrodes by the method previously described (p. 1456). Three different specimens of sesquioxide were used, (1) made by fractional precipitation from alkaline solution, (2) by the hypochlorite method, and (3) by the plumbate-plumbite method. Electrode (4) was made from pure sesquioxide (1) and stabilised electrolytic dioxide deposited on platinum.

Hydrogen scale. Temperature 17° (approx.).

Time after setting up (in days).									
No.	0	1	2	4	5	7	9	14	Final.
1	0.344	0.344	0.340	0.334	0.322	0.316	0.306	0.302	0.302
2	0.336					0.302	0.300	0.300	0.300
3	0.330					0.302		0.302	0.302
4	0.390	0.338		0.302				0.302	0.302
								Mean	0.302 volt.

The very high initial values are probably due to the presence of very small amorphous, almost colloidal, particles.

Lead sesquioxide is evidently, like red lead, a plumbous salt. The most reasonable structure for the former oxide is the one suggested by Bellucci and Parravano (*loc. cit.*),  $\text{Pb}^{\text{II}}\text{Pb}^{\text{IV}}(\text{OH})_6$ ; the positive ion is thus  $\text{Pb}^{\text{II}}$ , and the negative,  $\text{Pb}(\text{OH})_6^{\text{--}}$ . The electrode,  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO} \end{smallmatrix} \right| \text{N-NaOH}$ , should have given a more or less definite plumbate-plumbite potential, but in the presence of such a large amount of plumbite (since solid monoxide is present) very little sesquioxide will dissolve, only to be converted immediately into red lead (see below). The plumbate-plumbite potential would thus be entirely absent or extremely small.

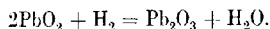
Since the potential of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right| \text{N-NaOH}$  half-element is 0.325 volt, and that of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \\ \text{PbO}_2 \end{smallmatrix} \right| \text{N-NaOH}$  half-element is 0.302 volt, and the  $\text{Pb}^{\text{II}}$ -ion concentration in the former is  $2.2 \times 10^{-17}$  gram-ion per litre, then in the latter case it is  $1.38 \times 10^{-16}$ . The plumbous-ion concentrations produced by dissolving the three oxides of lead in *N*-sodium hydroxide are  $2.2 \times 10^{-15}$  for the monoxide,  $1.38 \times 10^{-16}$  for the sesquioxide, and  $2.2 \times 10^{-17}$  for red lead. There will thus be a tendency for monoxide and sesquioxide to dissolve and form red lead, provided that lead dioxide and monoxide respectively are present in addition. This was verified by allowing some sesquioxide to stand in contact with a solution of lead monoxide in alkali; after six weeks both colour and analysis indicated



complete conversion of the oxide into red lead. Milbauer (*Chem. Ztg.*, 1914, **38**, 587) showed that lead monoxide and dioxide will combine in the presence of very strong alkali to form red lead. This reaction will also take place in the presence of *N*-sodium hydroxide, the sesquioxide probably being an intermediate stage. This subject will be dealt with in a further communication on lead dioxide.

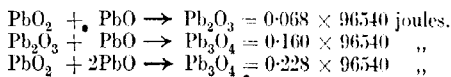
*Dissociation Pressures.*—Reinders and Hamburger (*loc. cit.*) found that the products obtained by the action of hypochlorite on alkaline plumbite gave exactly the same dissociation pressures as solid solutions of lead monoxide and dioxide of the same composition. The reason for this is that when the sesquioxide is heated, the water which is an integral part of the molecule is driven off, and a mixture (or solid solution) of monoxide and dioxide is left, since the anhydrous sesquioxide probably does not exist. This was shown by heating the sesquioxide at 200° for some time; on digesting the residue with a solution of sodium hydroxide, a considerable amount of lead monoxide was found to have dissolved. This could only have resulted from the decomposition of the sesquioxide by heat. No attempt has therefore been made to calculate dissociation pressures.

*Free Energy Relations.*—The cell  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3, 3\text{H}_2\text{O} \\ \text{PbO}_2 \end{smallmatrix} \right| N\text{-NaOH} \text{ H}_2(1 \text{ atm.}) | \text{Pt}$  has an *E.M.F.* of 0.302—(–0.810), that is, 1.112 volts at 17°, and the reaction involved is



The free energy of this reaction is therefore  $1.112 \times 2 \times 96540$  joules. Utilising this value, as well as the free energy values calculated on p. 1459, and assuming the free energy of the reaction,  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ , to be  $1.232 \times 2 \times 96540$  joules, the following results are obtained.

Free energy of the reaction :



#### Summary.

(1) Red lead and hydrated lead sesquioxide have been shown to be plumbous salts, giving plumbous ions in solution.

(2) No evidence has been found for the existence of an anhydrous sesquioxide.

(3) The existing methods for preparing the sesquioxide have been shown to be uncertain, and a new method has been worked out.

(4) The plumbate-plumbite-hydroxyl-ion equilibrium has been studied.

(5) The normal plumbate-plumbite potential has been found to be 0.30 volt at the ordinary temperature.

(6) The affinity relationships of lead monoxide, dioxide, sesquioxide, and red lead have been determined.

The author's best thanks are due to Professor A. J. Allmand for his interest in the work and for very helpful criticism and advice.

UNIVERSITY COLLEGE, EXETER.

[Received, May 3rd, 1922.]

CLXXIII.—*Physical Chemistry of the Oxides of Lead.*  
*Part V. The Electromotive Behaviour of Lead Dioxide.*

By SAMUEL GLASSTONE.

DURING the course of the work described below, the electromotive behaviour of ordinary chemical lead dioxide was compared with that of the dioxide deposited electrolytically from neutral or acid lead nitrate solution, and of the so-called hydrated lead dioxide deposited from slightly alkaline lead tartrate solution. The system lead-lead dioxide having been found to be unstable, measurements were made on the plumbic-plumbous electrode,  $\text{Pt} \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \text{N. NaOH}$ , where the lead dioxide was either introduced as a powder or deposited on a smooth or platinised platinum electrode. The electromotive behaviour of all the electrolytic products was the same, there being no distinction between the deposits from alkaline, neutral, or acid solution. In each case, however, there was evidence for the existence of an unstable higher oxide of lead, traces of which were present in solid solution in the dioxide. These results rendered desirable a redetermination of the normal plumbic-plumbous potential first measured by Cumming (*Trans. Faraday Soc.*, 1907, 2, 199), who used electrolytic lead dioxide.

EXPERIMENTAL.

The chemical lead dioxide used in this work was prepared (unless otherwise stated) by the action of bleaching powder solution on a boiling solution of lead acetate; the product was washed with hot dilute nitric acid and with water, and dried.

*The System Lead-Lead Dioxide.*

For the purpose of electromotive measurements it was desirable to know whether the system lead-lead dioxide was stable in the

presence of alkali. To test this, lead dioxide was mixed with pure spongy lead (made by the action of zinc dust on lead acetate solution and freed from excess of zinc) and kept in contact with 15 per cent. sodium hydroxide solution for some months. The colour of the oxide became more and more red, and after six months analysis indicated the formula  $\text{Pb}_3\text{O}_4$ . The system lead-lead dioxide-alkali must therefore be regarded as unstable. This fact was further confirmed by potential measurements on a  $\text{Pb}|\text{PbO}_2$   $N$ - $\text{NaOH}$  electrode. Immediately after setting up, the potential was  $-0.559$  volt, which is that of  $\text{Pb}|\text{PbO}$   $N$ - $\text{NaOH}$ , showing that the first reaction was  $\text{Pb}^{++++} + \text{Pb} \rightarrow 2\text{Pb}^{++}$ , or  $\text{PbO}_2 + \text{Pb} \rightarrow 2\text{PbO}$ . On the next day the  $P.D.$  was  $0.296$  volt, all the lead which had been deposited on the platinum electrode having been dissolved. The potential remained constant at this value, which corresponds with that of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_2\text{O}_3 \\ \text{PbO}_2 \end{smallmatrix} \right| N\text{-NaOH}$  electrode; evidently the second reaction had been  $\text{PbO} + \text{PbO}_2 \rightarrow \text{Pb}_2\text{O}_3$ . By renewing the lead deposit on the platinum electrode from time to time, the potential eventually rose to  $0.320$  volt, which is that of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_2 \end{smallmatrix} \right| N\text{-NaOH}$  electrode, showing that the final reaction was  $\text{PbO} + \text{Pb}_2\text{O}_3 \rightarrow \text{Pb}_3\text{O}_4$ .

*The  $\text{Pt} \left| \begin{smallmatrix} \text{PbO}_2 \\ \text{PbO} \end{smallmatrix} \right| N\text{-NaOH}$  Electrode.*

Owing to the instability of the  $\text{Pb}|\text{PbO}_2$  electrode, the electromotive properties of lead dioxide were investigated in the plumbic-plumbous electrode,  $\text{Pt} \left| \begin{smallmatrix} \text{PbO}_2 \\ \text{PbO} \end{smallmatrix} \right| N\text{-NaOH}$ , since the dioxide in solution almost certainly gives a definite concentration of  $\text{Pb}^{++++}$  ions, whilst the monoxide gives a definite  $\text{Pb}^{++}$  ion concentration. In the preliminary experiments lead dioxide was mixed in separate electrode vessels with various forms of lead monoxide and with hydrated monoxide, in fortuitous amounts. The vessels were then filled with  $N$ -sodium hydroxide, smooth platinum electrodes were inserted, and the potentials measured from day to day, the vessels being gently shaken in the intervals. In every case the potential at room temperature was initially about  $0.27$  volt, remained almost constant for two or three days, and then decreased slightly. After two or three weeks, a distinct reddening of the solid was observed in all the half-cells, whilst in some cases a layer of red solid had formed on the sides of the vessel. At the same time the potentials of some of the electrodes became very erratic, whilst others had increased to  $0.31$ – $0.32$  volt. In view of previous work (this vol., p. 1456) the explanation of these phenomena is as follows. Lead monoxide

and dioxide combine to form red lead; if the original mixture contained excess of monoxide, the final potential would be erratic, since  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{Pb}_3\text{O}_4 \end{smallmatrix} \right|$  does not give a definite potential value; if the dioxide had been present in excess, the final potential would be that of the  $\text{Pt} \left| \begin{smallmatrix} \text{Pb}_3\text{O}_4 \\ \text{PbO}_3 \end{smallmatrix} \right| N\text{-NaOH}$  half-element, that is, of the order of 0.32 volt. These conclusions were confirmed by making up mixtures containing known proportions of monoxide and dioxide, and measuring the potential of the  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \right| N\text{-NaOH}$  half-element from day to day.

Measurements at room temperature (about 17°). Scale  $\text{H}_2|\text{N-H}'=0$ .

I. 3PbO:PbO <sub>2</sub> .		II. 2PbO:PbO <sub>2</sub> .				III. PbO:2PbO <sub>2</sub> .		
		(a)		(b)		(c)		
Days.	P.D.	Days.	P.D.	Days.	P.D.	Days.	P.D.	
0	0.271	0	0.273	0	0.274	0	0.278	
1	0.270	4	0.266	4	0.260	4	0.268	
3	0.268	5	0.265	7	0.260	25	0.266	
7	0.261	7	0.265	11	0.260	39	0.322	
10	0.258	14	0.258	20	0.272	53	0.321	
33	0.237	28	0.271	26	0.308	Final	0.321	
Erratic after this period.		30	0.308	40	0.316		19	0.297
		45	0.312	56	0.315		75	0.314
		60	0.316	Final	0.315		Final	0.314
		Final	0.316					

The forms of lead monoxide used were, red in Series I, II *a*, and III; reddish-brown in II *c*; yellow in II *b*. In Series I, where the potential had become erratic after thirty-three days, a red solid had formed on the sides of the electrode vessel. The remainder of the solid was emptied out, and fresh dioxide and *N*-sodium hydroxide put in; the potential was now found to be 0.312 volt, a value which suggests that the red solid was a mixture of red lead and lead sesquioxide.

Similar series of experiments using lead dioxide prepared by the action of nitric acid on red lead gave exactly similar results.

Allowing for the initial high values due to the presence of very small particles, the value of the  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \right| N\text{-NaOH}$  electrode potential is probably of the order of 0.27 volt; this result was confirmed by the measurements on electrolytic lead dioxide described below.

#### Electrolytic Lead Dioxide.

Holland (*Compt. rend.*, 1903, 136, 229; 1904, 138, 142) found that lead dioxide deposited electrolytically on a platinised platinum

anode from a slightly acid solution of lead nitrate does not agree in composition with the formula  $\text{PbO}_2$ . He weighed the deposits obtained from various known amounts of lead nitrate, and suggested that the substance formed is an oxide,  $\text{PbO}_x$ , where  $x$  is greater than 2 and increases as the lead nitrate solution becomes more dilute. In the most dilute solution examined (0.0106 gram of lead in 300 c.c. of solution) the ratio,  $\text{Pb}/\text{PbO}_x$ , was found to be 0.74; this would correspond with a value of about 4.5 for  $x$ . No suggestion was, however, made that all or part of this extra mass may be due to the presence of adsorbed or combined water (compare Wernicke, *Pogg. Annalen*, 1870, **141**, 109). Using smooth platinum electrodes, Hollard found that in every case almost pure lead dioxide was deposited independent of the concentration of the lead nitrate solution. In order to investigate the possible electromotive differences in the various electrolytic products, a number of smooth and platinised platinum electrodes were coated with lead dioxide by electrolysis of various solutions of lead nitrate. After half an hour's deposition with a current of 0.01 ampere, the electrodes were rapidly washed with water, then with *N*-sodium hydroxide, and placed in electrode vessels containing lead monoxide and *N*-alkali. The potentials were measured immediately, and variations carefully followed. Every form of electrolytically deposited lead dioxide showed the same peculiar behaviour independent of the electrode material, current density, time of deposition, and concentration of the lead nitrate solution. The potential was in every case initially very high, 0.69 to 0.49 volt (compare the value 0.27 volt for the ordinary dioxide); this decreased very rapidly at first, then more slowly with a distinct break in the rate of fall at 0.40 volt. After this, the slow decline of potential continued sometimes for days or weeks, depending on the amount of the electrolytic deposit, until in every case the final value was 0.268 volt, corresponding with the normal  $\text{Pt} \begin{array}{c} \text{PbO} \\ \text{PbO}_2 \end{array} \text{N-NaOH}$  potential. At this value, the potential remained constant apparently indefinitely, probably due to the very slow rate of combination of electrolytic dioxide with the monoxide in the formation of red lead. No visible change could be observed in the dioxide during the fall of potential from 0.69 to 0.268 volt. A typical example of the rate of fall of the electrode potential is given below; it should be stated that the initial value can have no definite meaning, because it must depend on the very small period of time that elapses between setting up the electrode and finding the balance point on the potentiometer. The initial rate of fall is so great that even a very small interval would cause an appreciable fall in the potential.

Time.	P.D.	Time.	P.D.	Time.	P.D.	Time.	P.D.
0	0.593	7½ mins.	0.477	71 mins.	0.420	5 days	0.326
1 min.	0.558	15 "	0.455	104 "	0.416	7 "	0.310
2½ mins.	0.534	19 "	0.445	177 "	0.412	10 "	0.294
3 "	0.520	28 "	0.434	8 hours	0.407	13 "	0.284
3½ "	0.512	37 "	0.430	25 "	0.362	20 "	0.272
6 "	0.492	54 "	0.426	2 days	0.346	28 "	0.268

*Initial Values.*—The initial value measured appeared to depend to some extent on the current density used in depositing the dioxide; for example, with a current density of 0.004 amp./cm.<sup>2</sup>, the initial potential was 0.59 volt, but with 0.1 amp./cm.<sup>2</sup> it was 0.70 volt. As explained above, these values can only be regarded as comparative.

*Breaks.*—In some cases there was an indication of a break at 0.49 volt, but this was not very definite, and may have been due to the normal diminution of the initial very high rate of fall. In every case, however, a break was noted in the vicinity of 0.40 volt, after which there was a steady fall to the normal value of 0.268 volt.

*Rate of Fall.*—This depended to a great extent on the amount of dioxide that had been deposited. In one case, after deposition for five minutes with a current of 0.02 ampere on a platinum surface of about 1 sq. cm., the final steady state was reached in eighteen hours. Where a platinised electrode had been used and dioxide deposited for two hours with the same current, the steady state was reached only after fifty-six days.

#### *Hydrated Lead Dioxide.*

Before describing further experiments on the electrolytic dioxide, reference must be made to the hydrated dioxide,  $H_2PbO_3$ , claimed to have been prepared by Wernicke (*Pogg. Annalen*, 1870, **139**, 132) by the electrolysis of an alkaline solution of lead tartrate. Schreber (*Wied. Annalen*, 1889, **36**, 662) suggested that the product obtained had the formula  $Pb(OH)_4$  or  $PbO_2 \cdot 2H_2O$ . Streintz and Neumann (*ibid.*, 1890, **41**, 97) confirmed Wernicke's results,\* and measured the potentials of the elements  $Pb|PbO_2$  (chemical) and  $Pb|H_2PbO_3$  in sulphuric acid, against zinc. \*The *E.M.F.*s of these cells were 2.41 volts and 0.96 volt respectively; it appears from this that the anhydrous oxide is metastable with respect to the hydrated form. Owing to the great instability of the system lead-lead dioxide, it is probable that the potential measured is not that of  $Pb|PbO_2$  or  $H_2PbO_3$  in sulphuric acid, but rather a plumbic-plumbous potential. In the case of chemical lead dioxide, the solution surrounding the electrode would soon become saturated with lead sulphate, and so a stable potential would rapidly result. The electrolytic product ( $H_2PbO_3$ ) is less reactive, probably owing to state

of division (compare the formation of red lead on p. 1472), and therefore the solution would become saturated with plumbous salt very slowly. The potential measured would thus depend on the time elapsing between setting up and measurement.

Attempts were made to prepare this hydrated oxide by Wernicke's method (*loc. cit.*). Unless the current density was very low and the liquid stirred from time to time, the difficulty was experienced that a basic salt separated round the anode owing to local diminution of the hydroxyl-ion concentration. Even when there was no visible formation of basic salt, some may have possibly been deposited with the dioxide on the anode. After drying in a desiccator, the composition of the product varied in different specimens; three samples gave the percentage loss on heating as 11.7, 10.8, and 10.0, respectively ( $\text{H}_2\text{PbO}_3$  requires loss on heating = 13.22 per cent.). The substance was therefore not a pure hydrate, and may have belonged to the same category as the electrolytic deposits of Hollard (*loc. cit.*). The electromotive activity of the Wernicke product was investigated in the same way, and the results obtained were identical with those given by electrolytic lead dioxide deposited from acid or neutral lead nitrate solution. In every case where the so-called hydrate was examined, the initial potential was about 0.6 volt, falling rapidly to 0.40 volt, and then more slowly to the stable value, 0.268 volt. The existence of a pure hydrated dioxide,  $\text{H}_2\text{PbO}_3$ , is doubtful, and it is very probable that the substance is merely electrolytic lead dioxide containing about 3 per cent. of adsorbed water, which it is known to retain very tenaciously. Although the existence of  $\text{H}_2\text{PbO}_3$  has by no means been disproved, yet considering its electromotive behaviour, its variable composition, and the fact that no salts of the type  $\text{M}_2^{II}\text{PbO}_3$  \* are definitely known, but only those of the type  $\text{M}_2^{II}\text{Pb}(\text{OH})_6$  which are derived from the very unstable  $\text{H}_2\text{Pb}(\text{OH})_6$  (Bellucci and Parravano, *Z. anorg. Chem.*, 1906, 50, 107), its existence seems improbable.

#### *Stability of the Initial Electrolytic Product.*

The following experiments refer to lead dioxide deposited from lead nitrate solutions; similar experiments with the Wernicke product gave similar results.

Evidently during electrolytic deposition a highly metastable substance is formed which decomposes rapidly in the presence of lead monoxide and alkali. A series of experiments was carried out with the object of determining the stability of the product in other reagents and under differing conditions. Lead dioxide was

\* See, however, Grube's work (*Z. Elektrochem.*, 1922, 28, 273), which appeared after this paper was written.

deposited electrolytically from a 5 per cent. lead nitrate solution containing a little nitric acid; the electrode was washed and subjected to some physical or chemical treatment. It was then placed in an electrode vessel containing lead monoxide and *N*-sodium hydroxide, and the potential measured. The treatment and results are tabulated below.

Treatment.	Initial <i>P.D.</i> (volt).	Remarks.
c. In 4 <i>N</i> -HNO <sub>3</sub> for 18 hours	0.44	No break at 0.40 volt.
c. In 4 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> " " "	0.43	Normal fall.
c. In 4 <i>N</i> -H <sub>2</sub> SO <sub>4</sub> and PbSO <sub>4</sub> for 2 hours	0.45	" "
c. In electrolytic bath for 1½ hours with current off	0.37	
c. In 5% lead nitrate for 1 hour	0.39	
c. In <i>N</i> -sodium hydroxide for 2 hours	0.48	Normal fall.
c. In slightly acid hydrogen peroxide for 1 hour	0.35	Rose to 0.44 volt in 13 mins. and then fell steadily.
d. In boiling water for 5 minutes	0.30	Fell to 0.276 volt in 3 hours.

The following experiments were also made. (i) The freshly deposited lead dioxide was made up into a plumbic-plumbous half-element by placing it in a vessel containing about 4*N*-nitric acid and 0.01*M*-lead nitrate; after three days, when the potential was only 0.01 volt higher than that given by stable lead dioxide, the electrode was removed and its potential measured in lead monoxide and *N*-sodium hydroxide; the initial value was 0.45 volt.

(j) The lead dioxide was deposited from a nitrate bath surrounded by boiling water; the initial potential was 0.432 volt.

(k) An electrode prepared in the normal way was washed with water, alcohol, and ether, and placed in a desiccator for eighteen hours; the initial potential was 0.483 volt, and the fall normal.

We thus see that the substance giving the high electrode potentials decomposes comparatively slowly in acids and alkalis, but rapidly by the action of heat or sodium plumbite solution. The explanation suggested is that all the forms of electrolytic dioxide contain a higher metastable oxide in solid solution. The amount of this higher oxide present must be very small, as it could not be detected by analysis; there might, even so, be sufficient to show pronounced electromotive activity.\* Owing to its dilution by a

\* Since this paper was written MacInnes and Townsend (*J. Ind. Eng. Chem.*, 1922, **14**, 420) have reported the estimation of lead by electrolytic deposition as dioxide, the latter being immediately estimated by the direct iodometric or oxalic acid method. Since the results are in excellent agreement with theory, the authors claim to have definitely established that no higher oxides can be present in the electrolytic deposit. It should, of course, be added that a higher oxide may be present in an amount insufficient to be detected by ordinary methods of analysis.



large excess of dioxide, the rate of decomposition of the higher oxide would be greatly decreased, and would become smaller as the concentration became less. Theoretically, therefore, the rate of fall of potential should gradually decrease, and the potential for pure lead dioxide should be approached asymptotically; qualitatively this is the actual behaviour. Apparently acids and alkalis do not affect the rate of decomposition, but as is to be expected, rise of temperature accelerates it. A curious result is that of experiment (i), where practically normal potential values were obtained in the nitric acid half-element, yet the same electrode gave very high metastable values in the alkaline half-element. Evidently the higher oxide of lead, for which the formula  $\text{PbO}_3$  is tentatively suggested, like most other higher oxides, is acidic (compare  $\text{PtO}_3$ , Wöhler and Martin, *Ber.*, 1909, 42, 3326), and therefore gives negative ions electromotively active with other negative ions, for example, plumbite and plumbate, but not with plumbous and plumbic ions, which would be present in the nitric acid electrode. The presence of a very small concentration of  $\text{Pb}^{\text{VI}}$  ions might account for the slightly higher results obtained in the nitric acid half-element before stability was attained.

Another possible explanation is that the initial high values are due to adsorbed oxygen (compare Elbs and Forssell, *Z. Elektrochem.*, 1902, 8, 760). A potential of 0.69 volt would require an oxygen pressure of about  $10^{19}$  atms., and although adsorption pressures are known to be great, yet they would scarcely be of this order of magnitude. Whilst standing in nitric acid, gas bubbles were observed to be coming from the electrolytic deposit, but this may have been due either to displacement of adsorbed oxygen, or to the decomposition of the higher oxide,  $\text{PbO}_3$ .

*The Break at 0.40 Volt.*—A potential of 0.40 volt corresponds with that of a reversible oxygen electrode at a pressure of about 1 atmosphere, in *N*-sodium hydroxide. A break at this point would be expected, for the rate of escape of oxygen from the electrode would become slower when it was being evolved at a pressure equal to that of the oxygen in the atmosphere. It has been found that electrolytic lead dioxide deposited on lead electrodes does not show this break, which may have been due, therefore, to an oxide of platinum. Decomposition of this oxide by nitric acid would explain why lead dioxide electrodes kept in nitric acid (see expt. [a], p. 1475) do not show a break at 0.40 volt.

#### *The Normal Plumbic-Plumbous Potential.*

In measuring the normal  $\text{Pb}^{\text{IV}} \rightarrow \text{Pb}^{\text{II}}$  potential, Cumming (*loc. cit.*), who used electrolytically deposited lead dioxide, and noted

that in nitric acid half-elements the potential first fell, then became steady for many hours, and finally diminished slowly and apparently indefinitely, used the first steady value and attributed the subsequent fall to the presence of impurities. In view of the results obtained in the present investigation with electrolytic dioxide in alkaline electrodes, the determination of the normal plumbic-plumbous potential was repeated, using chemical lead dioxide only. Half-elements were made up from nitric acid solutions of known concentration containing known amounts of lead nitrate, and excess of solid dioxide. The potential of a smooth platinum electrode inserted well into the solid was measured, after a week, against that of a normal calomel electrode, using a saturated solution of ammonium nitrate as intermediate liquid. The results were compared with those obtained with electrolytic dioxide in the same solutions, and it was found that, in general, when the first (apparent) steady state was reached, the potentials of the latter were about 0.02 volt higher than those given by the chemical dioxide. After several days, both types of electrode gave identical potential values. The normal  $\text{Pb}^{IV} \rightarrow \text{Pb}^{II}$  potential is calculated below from the results obtained with the chemical dioxide, use being made of Cumming's empirical formula for the plumbic-ion concentration in nitric acid solutions saturated with lead dioxide, namely,  $[\text{Pb}^{IV}] = [\text{HNO}_3]^4 [\text{H}_2\text{O}]^3 \times 2.4 \times 10^{-7}$  gram-ion per litre at  $25^\circ$ .

Measurements at  $25^\circ$ . Scale  $\text{H}_2|\text{N} \cdot \text{H}' = 0$ .

$\text{HNO}_3$	$\text{Pb}^{IV}$	$E$ (volts)	$E_0$ (volts)	$\text{HNO}_3$	$\text{Pb}^{IV}$	$E$ (volts)	$E_0$ (volts)
0.483 N	0.005 M	1.519	1.686	1.90 N	0.05 M	1.587	1.713
"	0.05	1.494	1.689	"	"	1.624	1.730
0.965	0.01	1.547	1.686	3.81	0.01	1.653	1.723
"	0.05	1.522	1.684	"	0.05	1.642	1.734
0.980	"	1.531	1.690	6.00	0.01	1.694	1.743
1.729	0.005	1.598	1.699	"	0.05	1.682	1.754
"	0.05	1.570	1.700				

The steady increase in the value of  $E_0$ , the normal plumbic-plumbous potential, may be due to three causes, (a) the failure of ammonium nitrate solution to eliminate diffusion potential at high nitric acid concentrations, (b) the solubility of lead dioxide in the more dilute solutions is smaller than that calculated by the Cumming formula, and (c) in concentrated acid solution the thermodynamic activity of the plumbous ions is very much smaller than unity. The first point was tested by using saturated potassium chloride solution as intermediate liquid, when identical results were obtained; no further method for testing this possibility could be found. With regard to the second possibility, it would appear from the results obtained that the solubility of lead dioxide in *N*-nitric acid is about

one-hundredth part of that calculated by the Cumming formula; in dilute solutions, however, owing to the greater degree of ionisation of the nitric acid, one would expect a relatively greater solubility instead of a very much smaller one. As regards the third point, Cumming (*loc. cit.*) has shown that in fairly dilute acid solution, for example, 0.897*N*-nitric acid, the ratio of the lead nitrate concentrations in 0.1 and 0.01 molar solutions is a good measure of the ratio of the plumbous-ion concentrations. In 4.22 *N*-acid, however, even at such low lead nitrate concentrations as 0.01 and 0.0001, the ratio of the plumbous-ion concentrations, instead of being 100 : 1, was 18 : 1 (this value has been calculated from Cumming's *P.D.* measurements). This discrepancy is also seen in the results of the present series of measurements; with 3.81*N*- and 6.00*N*-acids, where the ratio of lead nitrate concentrations is 5 : 1 in each case, requiring a difference of potential of 0.021 volt, the actual differences are 0.011 and 0.012 volt, respectively. Further, if the Cumming formula is generalised in the form  $[Pb^{IV}] = [H]^4[H_2O]^2 \times 2.4 \times 10^{-7}$ , the normal plumbic-plumbous potential may be calculated from the known value of the  $Pt \begin{smallmatrix} PbO \\ PbO_2 \end{smallmatrix} N$ -NaOH electrode (0.268 volt). In this case, the  $Pb^{II}$ -ion concentration is known to be  $2.2 \times 10^{-15}$  (T., 1921, 119, 1914) and the  $Pb^{IV}$  concentration may be calculated from the above formula as  $2.2 \times 10^{-63}$ ; the normal  $Pb^{IV} \rightarrow Pb^{II}$  potential is thus 1.684 volts at 25°. This result is in striking agreement with those obtained in the more dilute nitric acid solutions.

Taking these facts into consideration, as well as the fact that electrolytic dioxide gives results that are probably slightly too high, the author is of opinion that the normal  $Pb^{IV} \rightarrow Pb^{II}$  potential, 1.82 volts, adopted by Cumming, is in excess of the true value. It is suggested that a potential of 1.75 volts at 25° would be more correct, although probably still too high. This value will be adopted in subsequent calculations.

#### *The Solubility Product of Lead Dioxide.*

From the known value of the potential of the  $Pt \begin{smallmatrix} PbO \\ PbO_2 \end{smallmatrix} N$ -NaOH electrode (0.268 volt), and of the plumbous-ion concentration produced by dissolving lead monoxide in *N*-sodium hydroxide ( $2.2 \times 10^{-15}$  gram-ion per litre), the plumbic-ion concentration in the electrode is  $1.30 \times 10^{-63}$  gram-ion per litre, assuming that the normal  $Pb^{IV} \rightarrow Pb^{II}$  potential is 1.75 volts. Since *N*-sodium hydroxide is dissociated to the extent of 72 per cent., the solubility product of the dioxide is given by

$$L_d = [Pb^{IV}][OH]^4 = 1.30 \times 10^{-63} \times (0.72)^4 = 3.25 \times 10^{-66}.$$

*The Instability of the System Lead-Lead Dioxide.*

If metallic lead is in contact with a solution containing  $\text{Pb}^{++++}$  and  $\text{Pb}^{++}$  ions, an equilibrium is set up as follows :

$\text{Pb}^{++++} + \text{Pb} \rightleftharpoons 2\text{Pb}^{++}$ . Hence, at equilibrium,  $[\text{Pb}^{++}]^2/[\text{Pb}^{++++}] = K$ .

This constant may be calculated from a consideration of the electrode potentials of the reactions  $\text{Pb}^{++} \rightarrow \text{Pb}$  and  $\text{Pb}^{++++} \rightarrow \text{Pb}^{++}$ ; when these potentials are equal, the system is in equilibrium. The normal electrode potentials are  $-0.130$  and  $1.75$  volts, respectively; hence, at equilibrium, we have :

$$1.75 + 0.0295 \log [\text{Pb}^{++++}]/[\text{Pb}^{++}] = -0.130 + 0.0295 \log [\text{Pb}^{++}]$$

whence  $[\text{Pb}^{++}]^2/[\text{Pb}^{++++}] = K = 10^{63.7}$ .

Suppose in this mixture of lead, plumbic, and plumbous ions solid lead dioxide is also present, then  $[\text{Pb}^{++++}][\text{OH}']^4 = L_4 = 10^{-66}$  (omitting the integers). When the system is in equilibrium,  $[\text{Pb}^{++}]^2[\text{OH}']^4 = KL_4$ , that is,  $[\text{Pb}^{++}][\text{OH}']^2 = \sqrt{KL_4}$ , which is equal to  $\sqrt{10^{-23}}$  (approx.).

In a solution saturated with lead monoxide (or hydroxide) the solubility product,  $[\text{Pb}^{++}][\text{OH}']^2 = 1.1 \times 10^{-15}$  (T., 1921, **119**, 1914); hence at equilibrium in the system lead-solid lead dioxide, the solubility product of the monoxide is very greatly exceeded ( $[\text{Pb}^{++}][\text{OH}']^2 = \sqrt{10^{-23}}$ ) and therefore this oxide will be precipitated. This will disturb the equilibrium, more  $\text{Pb}^{++++}$  ions will react with metallic lead to form  $\text{Pb}^{++}$  ions, which will again be removed from the system as solid monoxide, and these processes will continue until either all the solid lead is dissolved or only a minute amount of lead dioxide remains. These results demonstrate the essential instability of the system lead-lead dioxide.

*Dissociation Pressures.*

By considering the cell  $\text{Pt} \left| \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \right. N\text{-NaOH } \text{H}_2(\frac{1}{2} \text{ atm.}) \left| \text{Pt} \right.$ , the *E.M.F.* of which is  $0.268 - (-0.810) = 1.078$  volts at  $17^\circ$ , as an oxygen-hydrogen cell, the pressure of oxygen in the reaction  $\text{PbO}_2 \rightarrow \text{PbO} + \frac{1}{2}\text{O}_2$  may be calculated as  $2.4 \times 10^{-11}$  atm. Using the value 12,400 calories (Tscheltzow, *Compt. rend.*, 1885, **100**, 1458) as the heat of this reaction, the dissociation pressure calculated by Nernst's theorem is  $7.1 \times 10^{-12}$  atm. at  $17^\circ$ .

In view of the fact that lead dioxide on heating forms a series of solid solutions with the resulting lead monoxide (Reinders and Hamburger, *Z. anorg. Chem.*, 1914, **89**, 71), it did not appear desirable to make any detailed calculations as to the temperature of complete dissociation in air. One determination by the use of the integrated

form of the van't Hoff isochore gave a temperature of  $394^{\circ}$  for an oxygen dissociation pressure of 0.21 atm. By extrapolation from the results of Reinders and Hamburger, it appears that lead dioxide containing only a small amount of monoxide in solid solution would have a dissociation pressure about a hundred times as great, at that temperature.

*E.M.F.'s Calculated by Nernst's Theorem.*

The *E.M.F.* of the cell  $\text{Pt} \begin{smallmatrix} \text{PbO} \\ \text{PbO}_2 \end{smallmatrix} \text{N-NaOH H}_2(1 \text{ atm.}) | \text{Pt}$  involving the reaction  $\text{PbO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{PbO}$ , the water being in the form of ice, may be calculated for  $0^{\circ}$ . For the reaction at  $17^{\circ}$ , we have :

$$Q_r = 68,400 (\text{H}_2\text{O}) + 1580 (\text{ice, water at } 17^{\circ}) - 12,100 (\text{PbO, O}) \\ = 57,880 \text{ cal.}$$

The molecular heats of the reactants are 15.5 for the dioxide and 6.8 for hydrogen; those of the resultants are 11.8 for the monoxide and 9.5 for ice. These lead to a value of 57,228 cal. for  $Q_0$ , and  $-0.0043$  for  $\beta$ , from which the *E.M.F.* of the cell is calculated as 1.092 volts at  $0^{\circ}$ . By the more approximate method in which water is involved instead of ice,  $Q_0$  is found to be 56,880 cal., and  $\beta$  is  $-0.019$ , leading to an *E.M.F.* of 1.109 volts at  $17^{\circ}$ . The actual *E.M.F.* of the cell at  $17^{\circ}$  is 1.078 volts.

*Summary.*

(1) The stability of the system lead-lead dioxide in alkali has been investigated practically and theoretically.

(2) Electromotive measurements have shown that lead monoxide and dioxide combine in the presence of *N*-alkali to form red lead.

(3) The electromotive behaviour of electrolytically deposited lead dioxide suggests that a trace of a higher, acidic oxide (possibly  $\text{PbO}_3$ ) is present in the deposit.

(4) The evidence for the existence of a definite hydrated lead dioxide,  $\text{H}_2\text{PbO}_3$ , is criticised.

(5) The normal plumbic-plumbous potential has been redetermined, and a maximum value of 1.75 volts at  $25^{\circ}$  is indicated.

The author's best thanks are again due to Professor Allmand for his valuable suggestions and criticism.

UNIVERSITY COLLEGE,  
EXETER.

[Received, May 18th, 1922.]

CLXXIV.—*The Oxidising and Reducing Properties of Sulphur Dioxide. Part I. Mercury Chlorides.*

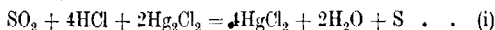
By LACHLAN MACQUARIE STEWART and WILLIAM WARDLAW.

THAT sulphur dioxide can function either as an oxidising or a reducing agent has been shown in the case of certain chlorides, sulphates, and phosphates (T., 1920, 117, 1093, 1241; this vol., p. 210). The concentration of the acid plays an important part in many of these reactions, for by varying the amount of acid present the sulphur dioxide can be made either to oxidise or to reduce.

The chlorides of mercury seem to afford an interesting case for investigation, for the fact that mercuric chloride is quantitatively reduced by sulphur dioxide to the mercurous salt only under very specific conditions has been noticed by investigators since the time of Vogel and Wohler. Sartorius (*Annalen*, 1855, 96, 335) showed that the question of concentration of the initial mercuric chloride solution is of great importance in determining whether the yield of mercurous chloride shall be quantitative or not. He showed that when a solution of mercuric chloride (1:80), saturated with sulphur dioxide at 70–80°, is maintained at that temperature for a prolonged period, the yield of mercurous chloride is almost theoretical. This conclusion was confirmed by Bolley.

The most recent contribution to this subject was made by Sanders (*Z. angew. Chem.*, 1915, 28, 9), who concluded that the oxidation of sulphur dioxide by mercuric chloride takes place in accordance with equation (iv). It was quantitative, however, only when the solution contained not more than two grams of sulphur dioxide per litre. With greater concentrations, the gas escaped unoxidised from the boiling solution.

Smythe and Wardlaw (*Proc. Durham Phil. Soc.*, 1914, 5, 187) have shown that sulphur dioxide oxidises mercurous chloride quantitatively to the mercuric salt in accordance with the equation :



Evidently the reactions of sulphur dioxide with mercury chlorides are of a diverse nature, and the following experiments were carried out with the object of further investigating the conditions for these reactions.

## EXPERIMENTAL.

*Reactions of Mercurous Chloride with Sulphur Dioxide.*

The method used in studying the reaction quantitatively was as follows :

A definite weight of mercurous chloride was covered with a known volume of hydrochloric acid of varying concentration containing dissolved sulphur dioxide, the mercurous chloride being white at this stage of the experiment. The flask was immersed in an oil-bath maintained at a constant temperature of 95°, and a slow stream of sulphur dioxide was passed through the mixture for twelve hours. The residue was filtered on a Gooch crucible, washed with dilute hydrochloric acid and with water respectively, dried, and weighed. The preliminary washing with hydrochloric acid removed sulphur dioxide which would have otherwise reduced the calomel to mercury on washing with water. The contents of the crucible were then extracted with chloroform in a Soxhlet tube, the sulphur being recovered by evaporation of the chloroform and weighed.

TABLE I.

Weight of mercurous chloride = 2.9376 grams.  
Duration of experiment = 12 hours.

Normality of hydrochloric acid.	Unchanged mercurous chloride. Grams.	Sulphur.		Remarks.
		Calc. Gram.	Found. Gram.	
8.64	nil.	0.0998	0.0989	No darkening.
4.75	1.9040	0.0351	0.0363	"
4.32	2.1408	0.0271	0.0293	"
2.16	2.6862*	0.0085	0.0070	Slight darkening.
1.73	2.7674	0.0058	0.0045	Appreciable darkening.
1.44			nil.	Appreciable darkening and no sulphur.

\* Duration, 7 hours.

The first point of note in connexion with these experiments is the fact that mercurous chloride remains white in the presence of sulphur dioxide and high concentrations of hydrochloric acid. Had the hydrochloric acid, initially employed, not contained sulphur dioxide, the acid alone would have decomposed the mercurous salt. Richards (*Z. physikal. Chem.*, 1897, **24**, 39) observed that mercurous chloride is appreciably decomposed into mercuric chloride and mercury in the presence of other chlorides, and Richards and Archibald (*ibid.*, 1902, **40**, 385) found that the system reaches a definite equilibrium and that the amount of mercuric chloride in the solution increases with increase in the chloride concentration, the increase being approximately proportional to the square of the concentration of the chlorine ions in the solution. If mercurous chloride is covered with sulphurous acid alone and warmed at 95°, darkening immediately occurs. Evidently, therefore, in our experiments with high concentrations of acid, the normal







the facts first recorded by Sartorius and mentioned in the introduction to this communication. The influence of the hydrochloric acid liberated in the reduction, however, requires consideration in view of the small ionisation of mercuric chloride even in aqueous solution, and especially on account of the formation of complexes with this acid. Le Blanc and Noyes (*Z. physikal. Chem.*, 1890, 6, 401) showed that the complex  $\text{H}_2\text{HgCl}_4$  is formed from mercuric chloride and hydrochloric acid and that it is a strong acid dissociating to about the same extent as hydrochloric acid.

With the object of determining the influence of concentration of hydrochloric acid on the reduction of mercuric chloride by sulphur dioxide, the experiments recorded in Tables III and IV were carried out. Sulphur dioxide was passed for twelve hours through a solution of mercuric chloride in 120 c.c. of standard hydrochloric acid at 95°.

TABLE III.

Normality of hydrochloric acid = 0.48N.

Mercuric chloride. Grams.	Mercurous chloride produced. Grams.	Mercuric chloride. Grams.	Mercurous chloride produced. Grams.	Remarks.
5.1580	0.1058	1.0106	0.0070	Crystalline deposits of calomel were formed in every experiment and no darkening was observed.
2.9760	0.0278	0.3090	0.0020	
1.8968	0.0160			

TABLE IV.

Normality of hydrochloric acid = 2.64N.

Mercuric chloride. Grams.	Remarks.	Mercuric chloride. Grams.	Remarks.
9.8314	No precipitate at the end of the experiment	36.2810	Very minute deposit, thought to be sulphur.
14.7352	"	46.3700	
25.7948	"	62.8170	

With a definite concentration of acid, the yield of mercurous salt is dependent on the concentration of mercuric chloride present.

TABLE V.

In the undermentioned experiments two solutions, having either a constant acid or a constant mercuric chloride content (the values bracketed in the table), were subjected, concurrently, to the action of sulphur dioxide for a definite period, which differed in the various experiments.

Temperature = 95°.

Mercuric chloride, Grams.	Concentrated hydrochloric acid, C.c.	Water, C.c.	Mercurous chloride obtained, Grams.
{ 3.3	5	115	0.0757
{ „	10	110	0.0063
{ 3.3	6	114	0.0245
{ „	9.6	110.4	0.0090
{ 6.6	4.8	115.2	0.4397
{ 3.3	„	115.2	0.0870
{ 6.6	4.8	115.2	0.2633
{ 13.2	„	115.2	2.0852

These experiments confirm the idea that the amount of mercurous chloride deposited is dependent on the concentration of the acid itself and the initial concentration of the mercuric chloride. Debray (*Compt. rend.*, 1882, **94**, 1222) observed a similar behaviour of mercuric chloride in solutions of sodium chloride. This peculiarity of mercuric chloride in the presence of hydrochloric acid and alkali chlorides seems satisfactorily explained by the fact that mercuric chloride is only slightly ionised even in aqueous solution and that it forms complexes with hydrochloric acid and alkali chlorides. Before reduction of the mercuric chloride can occur, a certain concentration of free mercuric ions must be present. In hydrochloric acid of high concentration, no such mercuric ions will be formed. When mercuric chloride is taken up in the form of the complex, it will ionise mainly as  $\text{H}_2\text{HgCl}_4 \rightleftharpoons 2\text{H}^+ + \text{HgCl}_4^{2-}$ . Le Blanc and Noyes (*loc. cit.*) have shown that the actual hydrogen-ion concentration of hydrochloric acid is unaffected by addition of mercuric chloride. However, the concentration of the chlorine ion is affected by the formation of the complex, and as this is the important ion in determining the ionisation of the mercuric chloride into mercuric ions, it follows that a stage will be reached in the addition of the mercuric chloride to the acid when the chlorine-ion concentration will be sufficiently lowered to allow the necessary mercuric ion concentration to be present for reduction to proceed. Obviously, on this view, the conditions for reduction are, in agreement with the experimental results, dependent on the concentration of the acid and of the mercuric chloride.

#### *The Quantitative Reduction of Mercuric Chloride.*

Sulphur dioxide was passed for twelve hours into an aqueous solution (120 c.c.) at 95° containing the amount of mercuric chloride given in the first column in Table VI.

TABLE VI.

Mercuric chloride. Grams.	Mercurous chloride. Grams.		Mercuric chloride. Grams.	Mercurous chloride. Grams.	
	Calc.	Found.		Calc.	Found.
3.3791	2.9380	2.8862	2.6053	2.2650	2.2470
3.3000	2.8690	2.8236	2.5990	2.2600	2.2400

From the above figures it will be seen that the reduction is nearly quantitative when 2.6 grams of mercuric chloride are present under the special conditions of the experiment. Sartorius found that reduction was nearly quantitative at 70–80° in a solution containing 1 gram of mercuric chloride in 80 c.c. Sanders (*loc. cit.*), using boiling solutions, found that the reduction was quantitative only when not more than 2 grams of sulphur dioxide per litre were present. This corresponds with a reduction of 17 grams of mercuric chloride per litre. Our figure corresponds with 21.7 grams of mercuric chloride per litre reduced by sulphur dioxide. Reference to Table VI, however, indicates that reduction would only be complete in a somewhat lower concentration of mercuric salt. On Sanders's figure, the reduction results in the liberation of hydrochloric and sulphuric acids, the total concentration of which produces an acidity of 0.13*N*. Undoubtedly the production of a definite acidity brings the reaction to a close, for hydrochloric acid will react with the mercuric chloride to form complexes and un-ionised molecules.

To determine what effect approximately 0.13*N*. or less concentrated hydrochloric acid has on calomel, the following experiments were carried out.

TABLE VII.

The mercurous chloride was covered with 120 c.c. of the acid of strength specified in the first column, and sulphur dioxide was passed for varying periods, the temperature being 95°.

Normality of hydrochloric acid.	Remarks.
0.160	No darkening at the end of 2½ hours.
0.020	Slightly grey at the end of 5 hours.
0.016	Dark at the end of 4 hours.
0.001	Distinctly black at the end of 4 hours.

These results serve to clarify those of Table II. Considering the results in Tables II and VII, it seems clearly established that in the reactions of mercurous chloride and sulphur dioxide in the presence of hydrochloric acid there is a definite stage of acid concentration where the calomel remains unaffected. The lower limit of this stage has been fixed by the experiments recorded in Table VI. The concentration of the hydrochloric acid liberated in the quantitative reduction of mercuric chloride was 0.065*N*; a similar concentration of sulphuric acid would also be liberated. With

concentrations of acid ranging from this to about 0.02*N*, only very slight darkening was detected. With acid less concentrated than 0.02*N*, distinct reduction was noted, which became more pronounced as the acid reached zero concentration. This reduction takes place in accordance with equation (iii).

Above 0.065*N*-acid concentration, there is a range of acidity where the calomel is unaffected. Beyond this area, darkening occurs in accordance with equation (ii).

*Reduction of Mercurous Chloride to Mercury.*

To determine the acidity produced when mercurous chloride was quantitatively reduced to mercury by sulphur dioxide, calomel, covered with water, was subjected to the action of sulphur dioxide at 95° for twelve hours. It was found that the maximum amount of calomel that was quantitatively reduced to mercury under the conditions of the experiment was 0.2024 gram. The maximum amount of mercuric chloride (in 120 c.c. of water) that was reduced to mercury by sulphur dioxide under the same conditions was 0.154 gram. Calculating the acidity of the solutions produced by the reductions, it was found that the mercurous salt gave a 0.014*N*-acidity and the mercuric chloride a 0.019*N*-acidity. These results show a distinct agreement and seem to indicate that for complete reduction a very low acid concentration must be finally produced.

From these results it would seem that if an acidity of more than approximately 0.02*N* is developed in the reduction of the mercury chlorides, reduction to mercury will be incomplete. Reference to the various results obtained in the investigation of the influence of acid concentration on the reduction of calomel shows that only when the acidity was less than the above figure was appreciable darkening noted. Superficial darkening has been noticed in acid of higher concentration, but it may be due to experimental error and not to a definite reduction effect.

*Summary.*

The type of reaction that occurs when sulphur dioxide reacts at 95° with mercurous chloride in the presence of hydrochloric acid depends on the concentration of acid present.

Normality of hydrochloric acid.	Remarks.	Equation.
8—2	<i>Oxidation area.</i> Oxidation decreases with decreasing acid concentration.	(i)
2—0.16	<i>Decomposition area.</i> Darkening decreases with decrease in acid concentration.	(ii)
0.16—0.07	<i>Inert area.</i> Calomel unaffected.	
0.07—0.02	Minute reduction.	
0.02—zero	<i>Reduction area.</i> Reduction increases with decreased acid concentration.	(iii)

Quantitative reduction to mercurous chloride occurs when sulphur dioxide reacts for twelve hours at 95° with approximately 2.6 grams of mercuric chloride in 120 c.c. of water. Above this concentration of mercuric chloride, incomplete reduction occurs. The amount of reduction of mercuric chloride to mercurous chloride depends on the concentration of hydrochloric acid present and the initial concentration of mercuric chloride.

The small degree of ionisation of mercuric chloride in aqueous solution, and the fact that it forms complexes with hydrochloric acid, have an important bearing on the above reactions.

The authors desire to express their thanks to the Chemical Society for a grant which has partly defrayed the expense of this investigation.

DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY, BIRMINGHAM.

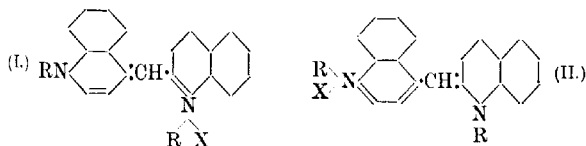
[Received, May 13th, 1922.]

### CLXXV.—*The Cyanine Dyes. Part V. The Virtual Tautomerism of the Thiocyanines.*

By WILLIAM HOBSON MILLS and WALTER THEODORE KARL  
BRAUNHOLTZ.

THE structural formulæ which have been established for various classes of cyanine dyes all contain one equivalent of an acid radicle and two nitrogen atoms of basic function connected by a chain of conjugate double linkings. This strongly suggested the possibility that these dyes might exhibit a type of virtual tautomerism involving the transference of the acid radicle from one of the two nitrogen atoms to the other with the correlated shift in the conjugated double linkings of the connecting chain.

Other considerations pointed in the same direction. For example, whilst the results of the oxidation of an isocyanine by potassium permanganate (Mills and Wishart, T., 1920, **117**, 579) indicate that the isocyanines have the structure II,

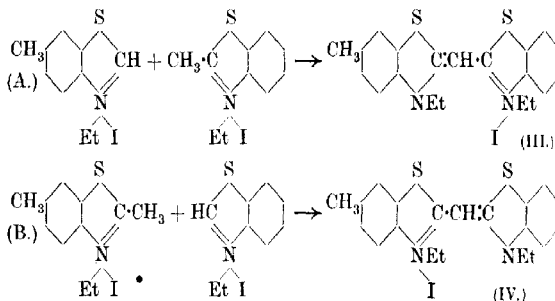


it is not easy to see how the direct formation of a substance of this constitution could take place through a condensation between a quinolinium pseudo-base and a quinaldinium salt in which the

methyl group of the latter was concerned; yet there is much reason to believe that the production of isocyanines by the action of alkali on a mixture of alkyl iodides of quinoline and quinaldine is dependent on a reaction of this kind. If, however, it could be assumed that the isocyanines were derived from a primary product of constitution I (König's formula) by an intramolecular change of the type suggested, this difficulty would be removed.

We have therefore investigated the question experimentally and have found that this type of virtual tautomerism actually exists; for identical cyanine dyes are formed in two processes which, in the absence of such an intramolecular change, should have given isomeric compounds, differing in the nitrogen atoms to which the acid radicle was attached.

The recently described thiocyanines (this vol., p. 454), derived from benzothiazole, are well adapted, as regards their constitution and method of formation, for investigation in this manner, and we have employed for our experiments compounds belonging to this group. We have condensed (i) 5-methylbenzothiazole ethiodide with 1-methylbenzothiazole ethiodide (reaction A) and (ii) 1:5-dimethylbenzothiazole ethiodide with benzothiazole ethiodide (reaction B) by heating together in pyridine solution.



If the thiocyanines are not virtually tautomeric compounds these two reactions should give different products, corresponding with the two formulæ III and IV.\* Careful examination showed, how-

\* If the thiocyanines were formed from an intermediate compound of the type  $\text{C}_6\text{H}_4\text{---}\langle\text{S---NEtI}\rangle\text{---C---CH}_2\text{---C}\langle\text{S---NEtI}\rangle\text{---C}_6\text{H}_4$  (by loss of hydrogen iodide), the identity of the products of the two reactions would be explained without the assumption of intramolecular change; for the same intermediate compound would then be formed by both pairs of alkyl iodides. The improbability that the condensation of the two alkyl iodides should precede the elimination of hydrogen iodide is, however, so great that we believe that this alternative need not be taken into account.

ever, that the thiocyanines formed were identical. Not only was there found to be exact correspondence in the general characters, the melting points, the melting point of the mixture, and the solubility of the two products, but it was also found that neither would dissolve in the saturated solution of the other.

Which of the formulæ, III or IV, is to be assigned to the crystalline product to which both of the reactions give rise has not been determined. It will evidently be the salt derived from the stronger of the two corresponding bases and therefore on account of the well-known influence of methyl groups on the strength of bases, the constitution IV must be regarded as the more probable. In view of the close correspondence in properties between the various classes of cyanine dyes, this demonstration of the virtual tautomerism of the thiocyanines can leave little doubt that the other classes of this group of dyes, the cyanines and carbocyanines and their respective isomerides, are capable of showing the same phenomenon.

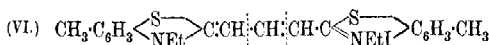
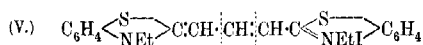
The tautomerism of the thiocyanines is evidently dependent on the association of the acid radicle in these compounds with a pair of nitrogen atoms connected by a chain of conjugated double linkings. We believe that it may safely be concluded that this phenomenon is not confined to the cyanine group of dyes, but will be exhibited by other types of ammonium salts in which these conditions recur, as, for example, the basic dyes of the triphenylmethane series.

In these condensations of benzothiazole alkylidides, brought about by boiling with pyridine, purple carbothiocyanines are formed along with the yellow thiocyanines. The composition of the carbothiocyanines produced in the two reactions described in this communication confirms the view of the origin of these compounds which has already been put forward (*loc. cit.*). According to this, the carbothiocyanine molecule contains the residues of two molecules of the 1-methyl-substituted benzothiazole alkylidide employed in the condensation, and these are linked together (as is indicated by the dotted lines in formulæ V and VI) by a methenyl group produced from, or by the agency of, the other alkylidide in which the 1-position is free.

The carbothiocyanine produced in reaction A, in which 1-methylbenzothiazole ethiodide and 5-methylbenzothiazole ethiodide were heated together in pyridine solution, was the same as that formed from benzothiazole ethiodide and 1-methylbenzothiazole ethiodide. This substance therefore clearly cannot contain a 5-methyl group; the two benzothiazole nuclei which it contains are consequently both derived from the alkylidide which contains the 1-methyl



group, and the substance in all probability possesses the constitution V.



Reaction B gives rise similarly to 5:5'-dimethyl-2:2'-diethyl-carbothiocyanine iodide. It has already been shown (*loc. cit.*) that this fact leads to the same view of the method of formation of the carbothiocyanines.

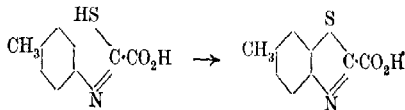
#### EXPERIMENTAL.

##### (A.) Condensation of 5-Methylbenzothiazole Ethiodide with 1-Methylbenzothiazole Ethiodide.

**5-Methylbenzothiazole.**—This base was first obtained by Hess (*Ber.*, 1881, **14**, 492) by heating *p*-aminothio-*m*-cresol with formic acid. We have prepared it by the decomposition of 5-methylbenzothiazole-1-carboxylic acid, a method analogous to that by which Reissert (*Ber.*, 1904, **37**, 3731; 1905, **38**, 3430) obtained benzothiazole.

Ethyl oxatoluidate (20 grams), obtained from ethyl oxalate and *p*-toluidine (Klinger, *Annalen*, 1877, **184**, 285), was dissolved in xylene (200 c.c.) and the solution boiled with phosphorus pentasulphide (6 grams) for one hour. The mixture was filtered through glass wool to remove tarry matter, and the reddish-brown xylene solution extracted three times with 10 per cent. aqueous sodium hydroxide. On acidifying the united extracts with hydrochloric acid, a bright yellow, crystalline precipitate of thionoxatoluidic acid was obtained, which was filtered, washed with a little cold water, and dried in an evacuated desiccator. The yield was about 10 grams. The acid was purified for analysis through its sodium salt (compare the preparation of thionoxanilic acid by Reissert, *Ber.*, 1904, **37**, 3712). The pure compound forms small, light yellow crystals, melting and decomposing at 134–135° (Found: N = 7.15.  $C_6H_5O_2NS$  requires N = 7.18 per cent.).

The oxidation of thionoxatoluidic acid by potassium ferricyanide



results in the formation of a benzothiazole ring. To a solution of

the acid (25 grams) in 5 per cent. aqueous sodium hydroxide (400 c.c.), a 20 per cent. aqueous solution of potassium ferricyanide (560 c.c.) was slowly added at room temperature with mechanical stirring. The sodium salt of 5-methylbenzothiazole-1-carboxylic acid, which began to separate almost immediately, was collected and washed with a little cold water. The filtrate, containing some of the sodium salt in solution, was acidified with hydrochloric acid, the free carboxylic acid being precipitated as an almost colourless solid. The sodium salt was dissolved in warm water (about 500 c.c.) and the solution filtered to remove a little tarry matter. On acidification with hydrochloric acid, the carboxylic acid was thrown down as a voluminous, colourless, crystalline solid, which was filtered and washed with a little cold water.

The united yield of 5-methylbenzothiazole-1-carboxylic acid was transferred, without further purification or drying, to a wide-necked flask and decomposed by warming under reflux. Frothing occurred owing to liberation of carbon dioxide, and water and a sweet-smelling oil remained. The latter was extracted with ether, the extract dried with anhydrous sodium carbonate, and the residue distilled under diminished pressure. 5-Methylbenzothiazole (11–12 grams) was thus obtained as an almost colourless oil of honey-like odour; it boiled at  $249^{\circ}/755$  mm., and at  $133^{\circ}/18$  mm. It solidified on cooling with ice and melted at  $15^{\circ}$  (Hess, *loc. cit.*, gives b. p.  $255^{\circ}$ , m. p.  $15^{\circ}$ ).

5-Methylbenzothiazole ethiodide was prepared by heating equimolecular quantities of the base and ethyl iodide in a sealed tube at  $100^{\circ}$  for eighteen hours. The crystalline mass formed was recrystallised from alcohol, giving colourless prisms melting at  $168^{\circ}$ , the yield being almost theoretical (Found: I = 41.86.  $C_{10}H_{12}NIS$  requires I = 41.64 per cent.).

*The Thiocyanine ( $T_1$ ).*—A solution containing 5-methylbenzothiazole ethiodide (5 grams) and 1-methylbenzothiazole ethiodide (5 grams) in pyridine (20 c.c.) was gently boiled for seven hours. After keeping the deep purplish-red reaction mixture for forty hours in a dark place, a red, crystalline solid was found to have separated. This consisted of a mixture of the unchanged ethiodides and the thiocyanine, coloured red by the presence of a trace of the carbothiocyanine. It was collected and the unchanged ethiodides were removed by extraction with warm water. The residual thiocyanine ( $T_1$ ) was purified by repeated crystallisation from methyl alcohol. It forms bright yellow needles, m. p.  $286^{\circ}$  (decomp.). Yield 0.4 gram (Found: C = 50.5; H = 4.34; I = 26.3.  $C_{20}H_{21}N_2IS_2$  requires C = 50.0; H = 4.37; I = 26.46 per cent.).

2:2'-Diethylcarbothiocyanine Iodide.—The pyridine filtrate con-

taining the carbothiocyanine was poured into about five times its volume of water. A dark, resinous precipitate was formed which, after digestion with ether, left the dye as a deep purple, amorphous solid. By crystallisation from methyl alcohol, the characteristic steel-blue prisms of 2:2'-diethylcarbothiocyanine iodide were obtained. Dried at 120–130°, the loss in weight was 6.31 per cent. ( $C_{21}H_{21}N_2IS_2 \cdot CH_3 \cdot OH$  requires  $CH_3 \cdot OH = 6.11$  per cent.). (Found: I = 25.98. Calc., I = 25.81 per cent.). The melting point was the same as that of the carbothiocyanine prepared from benzothiazole ethiodide and 1-methylbenzothiazole ethiodide, and the mixture of the two preparations also melted at the same temperature. As the carbothiocyanines decompose at the melting point, the melting point observed depends on the rate of heating. Heated very slowly in the same bath, the two products and their mixture each melted at 260°.

(B.) *Condensation of Benzothiazole Ethiodide with 1:5-Dimethylbenzothiazole Ethiodide.*

This condensation has already been described by one of us (*loc. cit.*). For the present purpose, a solution of benzothiazole ethiodide (6 grams) and 1:5-dimethylbenzothiazole ethiodide\* (8 grams) in pyridine (25 c.c.) was gently boiled for seven hours. The thiocyanine ( $I_2$ ) and the carbothiocyanine (5:5'-dimethyl-2:2'-diethylcarbothiocyanine iodide) were isolated and purified as described above.

The thiocyanine was obtained as bright yellow needles melting and decomposing at 286° (Found: C = 49.76; H = 4.37; I = 26.58. Calc., C = 50.0; H = 4.37; I = 26.46 per cent.).

*The Identity of the Thiocyanines Produced in the Two Condensations.*

The thiocyanines produced in the two condensations are indistinguishable in appearance. The composition of each, as has been shown above, agrees with the formula  $C_{20}H_{21}N_2IS_2$ . There is also exact concordance in the melting points; both products, as well as the mixture of the two, melted and decomposed at the same temperature (286°) when heated side by side in the same apparatus.

Finally, the identity of the two products was definitely established by determinations of their individual and mixed solubilities.

Excess of the substance (0.8 gram) was stirred continuously for several days with methyl alcohol (100 c.c.) in a thermostat at 25°. From time to time about 10 c.c. of the solution were withdrawn,

\* This salt, crystallised from rectified spirit, contains water of crystallisation and melts at 138°. The anhydrous salt melts at 163°.

weighed, and evaporated, and the weight of dissolved substance determined. The determinations gave the following results :

Duration of stirring (hours).	Dissolved thiocyanine (grams per 100 grams of solution).	
	$T_1$ .	$T_2$ .
44	0.243	0.240
67	0.242	0.234
95	0.238	0.250
119	0.239	0.242
163	0.237	0.241
Mean	0.240	0.242

Saturation was thus attained within the first forty-eight hours, and the solubility of the two products was the same within the limits of experimental error. The two saturated solutions, together with the undissolved solid in contact with each, were then mixed and the stirring was continued at 25°. Five determinations of the amount of dissolved substance were made at intervals between twenty-four and forty-eight hours after mixing. The values obtained were 0.242, 0.237, 0.238, 0.246, 0.243, giving a mean of 0.241 gram of dissolved thiocyanine per 100 grams of solution. Thus, neither of the two products  $T_1$  and  $T_2$  was able to dissolve in the mixture of their saturated solutions; they were therefore identical.

For comparison, the corresponding experiment was carried out with methyldiethylthiocyanine iodide ( $T_1$ ) and a different, but very closely related compound, diethylthiocyanine iodide.

	Gram per 100 grams of solution.
Methyldiethylthiocyanine iodide ( $T_1$ ) .....	0.240
Diethylthiocyanine iodide ( $T_2$ ) .....	0.123
Mixture of $T_1$ and $T_2$ .....	0.373

Here, as was to be expected, the solubility of the mixture of the two substances was equal, approximately, to the sum of their individual solubilities.

One of us (W. T. K. B.) is indebted to the Department of Scientific and Industrial Research for a grant for which he desires to express his thanks.

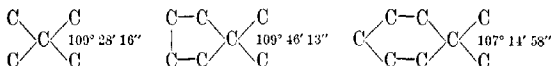
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CAMBRIDGE.

[Received, June 15th, 1922.]

CLXXVI.—*The Formation and Stability of spiro-Compounds. Part VIII. The Dieckmann-Komppa Reaction.*

By FRANK DICKENS, GEORGE ARMAND ROBERT KON, and  
JOCELYN FIELD THORPE.

THE evidence communicated in the previous parts of this series shows that when two of the valencies of a carbon atom are linked to two single carbon atoms which are themselves otherwise free, the angle subtended by the four valencies may be regarded as being equal to the normal tetrahedral angle, that is,  $109^{\circ} 28'$ , but that if the two carbon atoms are not free and are included, for example, in a *cyclohexane* complex, the angle is deflected and becomes in this case  $107^{\circ} 15'$ . On the other hand, the inclusion of these



carbon atoms in a *cyclopentane* complex was shown in Part III (T., 1920, 117, 1580) to lead to experimental results which were in accordance with the view that the angle in this case was  $109^{\circ} 46'$  and therefore differed only by a few minutes of arc from the normal angle.

Still more recently (this vol., p. 1430) it has been shown that even although the carbon atoms are not included in a ring the angle may be altered by linking another carbon atom to each of the two carbon atoms which influence the deflection of the angle. Thus the diethyl group was found to exert an influence which was, in effect, between that caused by the dimethyl group and *cyclohexane* ring.

The evidence was based for the most part on a close study of the three-membered carbon ring compounds which were formed from the diacetic acid in each series, and it has been clearly proved that, in this connexion, the deflexion of the angle increases both ease of formation and stability, and that the order of effect is that which is in accordance with the alteration of the angle, namely—

*cyclo*Pentane—*gem*-Dimethyl—*gem*-Diethyl—*cyclo*Hexane.

It follows that the methylethyl group will probably come between the *gem*-dimethyl and the *gem*-diethyl groups, an assumption which is not only borne out by the experiments described in this paper, but to which other experiments, shortly to be published, afford strong support.

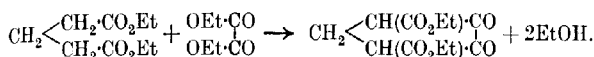
In the present paper we bring forward experimental evidence

which shows that the deflexion of the angle affects the formation of the five-membered carbon ring in a manner similar to that which is apparent in the *cyclopropane* series. The experiments have been carried out in the same way as that adopted in the previous series, namely, a reaction leading to the formation of a five-membered carbon ring has been chosen and the quantity of cyclic condensation product formed in each of the series mentioned below, under precisely similar experimental conditions, has been compared.

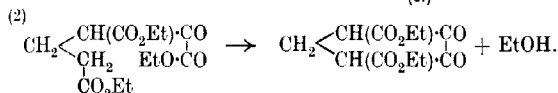
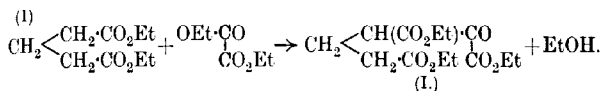
The reaction selected in the present instance was that originally discovered by Dieckmann (*Ber.*, 1894, **27**, 965) and by which he prepared derivatives of *cyclopentanedione* by the condensation of oxalic ester with an ester of a glutaric acid in the presence of sodium.

The reaction may be represented as proceeding in either one of two ways :

(a) It may be of the " box and lid " type and go in one stage :



(b) It may occur in two stages, an oxalyl derivative being the intermediate product :

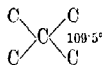
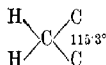


In the first place it was necessary, in order to make our proposed comparison complete, to ascertain in which way the reaction proceeded. It is evident that any tendency to five-carbon ring formation due to the deflection of the tetrahedral angle in the glutaric complex would be greater if the reaction were of type (a) than if it were of type (b) because in the former case the necessary alteration in valency direction would be borne by both carbon atoms of the oxalic ester group whereas, in a reaction of type (b), the whole change would have to be borne by a valency of one carbon atom.

As a matter of fact the experiments show that the course of the reaction is that represented by (b), and, in the case of the simplest member, we have been able to isolate the intermediate oxalyl derivative (I). The discovery that this is the true course of the reaction enabled us, moreover, to furnish an explanation of certain remarkable facts which were revealed by a study of the literature, and which, at first sight, seemed to conflict with the general hypo-

this forming the basis of this series of communications and which is given in outline on page 1496. For example, Dieckmann found that the greatest yield of condensation product was formed when ethyl glutarate was used, that a diminished yield was obtained with ethyl  $\beta$ -methylglutarate, and that only a poor yield of product could be isolated when ethyl  $\beta\beta$ -dimethylglutarate was employed.\*

It will be noticed that if the angles are of the order



and if the reaction is of the "box and lid" type (a), the greatest yield should have been given by  $\beta\beta$ -dimethylglutaric ester, in which the tetrahedral angle differs from the angle of the *cyclopentane* ring by some minutes of arc only. We have no reasons to doubt that the values given to the angles are substantially correct, and, if we had no experimental evidence to warrant us in doing so, we should have had to discard, on these grounds, the view that the reaction could proceed in accordance with type (a), but, as it happens, the proved course of the reaction provides us with an adequate explanation which brings into line with our general hypothesis the facts which seem to conflict with it.

It has already been mentioned that the greatest yield of condensation product is given by glutaric ester itself. It therefore follows that in the oxalyl derivative (1) the carbon atoms which are to join during the second stage of the reaction in order to form the five-membered ring must be nearer together than in any other member of the series. It follows also that this effect can only have been produced by the alteration of the "normal" angle of  $115.3^\circ$  to a value approaching that of the angle of the *cyclopentane* ring and that this result has been brought about by the presence of the oxalyl group on the  $\alpha$ -carbon atom.

What now would be the effect produced by a further deflexion of the angle due to the presence of *gem*-groupings or ring complexes? The effect would obviously be to produce an overlapping in the positions of the two carbon atoms which are required to link in order to produce the five-membered ring, with the result that the greater the deflection the greater would be the difficulty experienced in closing the ring, until a stage would be reached where the possibility of this particular ring formation would cease.

The experiments described in this paper support the hypothesis

\* Komppa (*Annalen*, 1900, **368**, 137) materially increased this yield by using a more strongly enforcing reaction. Komppa's modification of the Dieckmann reaction was used by us throughout.

mentioned above, for it is found that as the angle decreases the yield of *cyclopentanedione* decreases, a fact which is clearly shown by the following table :

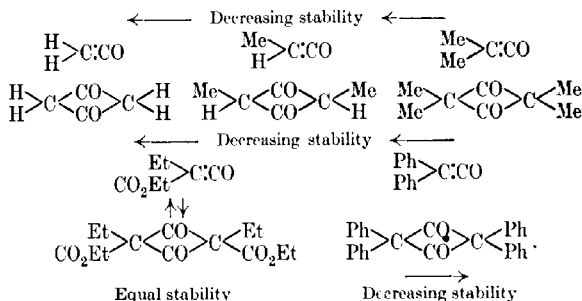
Oxalic ester with ester of	"Normal" angle.	Yield of <i>cyclopentanedione</i> .
Glutaric acid .....	115.3°	"Reichlich" 80 per cent.*
$\beta$ -Methylglutaric acid .....	112.5°	"Almost quantitative."*
<i>cyclo</i> Pentandiacetic acid.....	109.5°	60-70 per cent.
$\beta\beta$ -Dimethylglutaric acid ...	109.3°	66 per cent.†
$\beta\beta$ -Methylethylglutaric acid ..	— ‡	20 per cent.
$\beta\beta$ -Diethylglutaric acid .....	— ‡	Nil.
<i>cyclo</i> Hexandiacetic acid .....	107.2°	Nil.

\* Dieckmann.

† Komppa, also confirmed by us.

‡ We have no means, at present, of determining the influence of the ethyl group.

This assumption implies that, in a series such as that given above, the carbon atoms which join to form the five-membered ring have reached positions of closest proximity in the oxalyl derivative of the unsubstituted glutaric series, and that in the successive members, the distance between these two carbon atoms increases through overlapping. There are several experimental facts which support this view, but perhaps the most striking are those supplied by the investigations of Staudinger (*Ber.*, 1911, **44**, 521) on the polymerisation of the ketens, which are summarised in the following table :

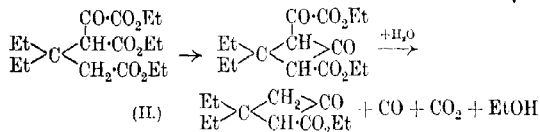


It will be noticed that the stability of the *cyclobutane* ring reaches a maximum in the dimethyl series and thereafter declines—a clear example of the effect of overlapping.

There are, moreover, certain other facts which arise from our experiments which can be adequately interpreted only on the assumption that overlapping of the kind postulated actually occurs. It will, for example, be realised that the increasing deflexion of the angle which leads to the increasing separation of the two carbon atoms required for five-membered ring formation must tend to bring



the two carbon atoms required for four-ring formation closer together. If, therefore, the compound under investigation is one which can lend itself equally well to four- or five-carbon ring production, it is to be expected that in those cases where the overlapping has separated the carbon atoms required for five-ring formation to a distance which prevents the reagent used from joining them, as, for example, in the diethylglutarate and *cyclohexanediacetate* series, evidence might be found showing that some, at any rate, of the four-carbon ring compound had been formed. As a matter of fact, the oxalyl derivative is a compound of the type described, for not only can it be transformed into the five-membered ring as shown on page 1497, but it can also be converted into a four-membered ring as indicated below:

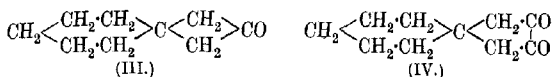


Oxalyl derivatives of this kind are, as is well known, readily hydrolysed and then pass into the monocarboxylic ester in the manner shown.

It is therefore to be expected that if any of the four-ring derivative is formed in the diethylglutarate and *cyclohexanediacetate* condensations, it will be found as the ester of the keto-monocarboxylic acid in the steam distillate.

Our experiments on this point are conclusive in so far as they show that a small quantity of the diethyl-keto-ester (II) is produced in the condensation of methyl  $\beta$ -diethylglutarate and methyl oxalate by the Komppa modification of Dieckmann's reaction, but, unfortunately, all attempts to isolate a similar compound in the *cyclohexanediacetate* series, which should, theoretically, give a larger yield of the *cyclobutane* derivative, were unsuccessful. When it is remembered, however, that the experimental difficulties which arise in the *cyclohexanediacetate* series are very much greater than those which have to be surmounted in the diethylglutarate series, owing, for example, to the less volatile character of the products formed, it is easy to understand how the small quantity of *cyclobutane* derivative which should have been produced could have been lost among the mass of uncrystallisable gum and resin which is the actual product of the interaction of methyl *cyclohexanediacetate* and methyl oxalate in the presence of sodium methoxide. We do not think, therefore, that too much stress should be laid on this one weak spot in our chain of evidence.

During our experiments with the ester of *cyclohexanediacetic* acid we noticed that the condensation with oxalic ester led to the formation of very small quantities of the mono-ketone (III) and of the diketone (IV).



These compounds have been prepared by Kon (this vol., p. 520) by the action of metallic potassium on ethyl *cyclohexanediacetate*, and it seemed to us likely that they might have been formed in our reaction in a similar manner, the oxalic ester having played no part in their production. This was proved to be the case, because an experiment carried out without oxalic ester was found to yield the same small quantities of the two ketones.

It is evident that it will be necessary, in order fully to establish the views advanced in this paper, to isolate the oxalyl derivative of each member of the series and to study the conditions under which they are transformed either into the four- or into the five-membered carbon ring. These experiments are now in hand and will form the subject of another communication.

#### EXPERIMENTAL.

##### *Condensation of Ethyl Glutarate and Ethyl Oxalate.*

The pasty mass formed, with evolution of heat, from ethyl oxalate (21.9 grams) and sodium ethoxide (prepared from 3.5 grams of sodium), was dissolved in dry ether (90 c.c.) and ethyl glutarate (28.2 grams) added with vigorous shaking. The mixture, having been gently boiled under reflux for twenty-four hours, was cooled with ice, and the yellow precipitate of sodium derivatives was collected, washed with ether, and decomposed with ice-cold, dilute sulphuric acid. The pale yellow oil produced, isolated by means of ether, weighed 18 grams. This oil contained about 50 per cent. of ethyl hydrogen glutarate; the remainder consisted of approximately equal weights of the *oxalyl* derivative (I) and ethyl *cyclopentane-3:4-dione-2:5-dicarboxylate*, the latter crystallising on keeping.

The oxalyl derivative was isolated in the form of its *semicarbazone*, which crystallises from alcohol as colourless needles melting at 130° (Found: C = 48.89; H = 6.94; N = 12.16.  $\text{C}_{14}\text{H}_{22}\text{O}_7\text{N}_3$  requires C = 48.70; H = 6.72; N = 12.17 per cent.).

On distillation, the oxalyl derivative decomposed quantitatively into carbon monoxide and ethyl propane- $\alpha\gamma\gamma$ -tricarboxylate, a colourless oil boiling at 184°/26 mm. (compare *Ber.*, 1891, 24, 282)

(Found: C = 55.35; H = 7.87. Calc., C = 55.35; H = 7.75 per cent.). The ester was readily hydrolysed by Bischoff's method (*Annalen*, 1882, **214**, 40) to *propane-xy-tricarboxylic acid*, small, colourless prisms melting at 123° after crystallisation from ether and petroleum (Found: C = 40.86; H = 4.67.  $C_6H_8O_6$  requires C = 40.91; H = 4.58 per cent.). The acid evolves carbon dioxide on heating above its melting point, and the residue consists of glutaric acid, identified by direct comparison with a genuine specimen.

#### *The Komppa Reaction.*

The condensation of methyl oxalate with the esters investigated was carried out exactly as described by Komppa (*loc. cit.*, p. 137). After acidification with ice-cold, dilute sulphuric acid, the treatment varied according to the nature of the product, which, in the case of methyl  $\beta\beta$ -dimethylglutarate and methyl cyclopentane-1:1-diacetate, was quite solid; whereas in the other cases investigated it was of an oily nature and therefore was isolated by extraction with ether.

*Methyl cyclopentane-1:1-diacetate.*—This ester is a colourless oil boiling at 162°/15 mm. (Found: C = 61.41; H = 8.62.  $C_{11}H_{18}O_4$  requires C = 61.63; H = 8.50 per cent.).

The crude condensation product obtained from 18 grams of the ester weighed 12 grams (60 per cent. yield), melted at about 125—130°, and was readily purified by crystallisation from alcohol.

*Methyl cyclopentanespirocyclopentane-3:4-dione-2:5-dicarboxylate*,  $\begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix} > C < \begin{matrix} CH(CO_2Me) \cdot CO \\ CH(CO_2Me) \cdot CO \end{matrix}$  separates in slender, colourless needles, melting at 138.5°, from benzene, ether, or dilute methyl alcohol. Like those of other similar ketonic esters, its alcoholic solution gives an intense port-wine coloration with ferric chloride; the ester dissolves in aqueous sodium hydrogen carbonate with effervescence (Found: C = 58.03; H = 6.14.  $C_{13}H_{16}O_6$  requires C = 58.18; H = 6.02 per cent.).

The *quinoxaline* derivative,  $C_4H_8 > C < \begin{matrix} CH(CO_2Me) \cdot \dot{C} : N \\ CH(CO_2Me) \cdot \dot{C} : N \end{matrix} > C_6H_4$ , was easily prepared by evaporating an alcoholic solution containing the calculated quantities of the diketonic ester and *o*-phenylenediamine. The oily residue solidified and was recrystallised from methyl alcohol, forming minute, primrose-yellow prisms melting at 215—216°. The substance is sparingly soluble in alcohol, giving a yellow solution with a green fluorescence (compare Dieckmann, *Ber.*, 1902, **35**, 3208) (Found: C = 67.02; H = 6.15.  $C_{19}H_{20}O_4N_2$  requires C = 67.00; H = 5.94 per cent.).

The diketonic ester was readily hydrolysed on boiling for two

hours with an excess of 20 per cent. sulphuric acid. The brown oil obtained solidified on cooling, and after pressing on porous tile, the substance was crystallised from aqueous alcohol, forming beautiful, silvery plates melting at about  $106^{\circ}$ . A second crystallisation from light petroleum (b. p.  $40-50^{\circ}$ ) raised the melting point to  $110-111^{\circ}$ , and the substance was shown to be identical with the *cyclopentanespirocyclopentane-3:4-dione* described by Kon (*loc. cit.*, p. 526) by direct comparison and by analysis (Found: C = 70.98; H = 8.10. Calc., C = 71.00; H = 7.96 per cent.).

The quinoxaline derivative was also prepared and was identical with that described by Kon (*loc. cit.*), melting at  $95-96^{\circ}$ .

*Methyl  $\beta$ -Methyl- $\beta$ -ethylglutarate*.—This ester boils at  $128^{\circ}/19$  mm. (Found: C = 59.10; H = 8.98.  $C_{10}H_{18}O_4$  requires C = 59.37; H = 9.00 per cent.).

Fourteen grams of the ester were used for each condensation. The product, which partly solidified after contact with ice-cold dilute sulphuric acid for several hours, was pressed on a porous tile and washed with a little benzene, when a nearly colourless solid remained. A small additional quantity could be obtained by extracting the tile with ether. The best yield was 3 grams of crude substance (19 per cent.).

*Methyl 1-methyl-1-ethylcyclopentane-3:4-dione-2:5-dicarboxylate*,  $\text{CH}_3 > \text{C} \begin{matrix} \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CO} \\ \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CO} \end{matrix}$ , forms short, thick, colourless needles, melting at  $126^{\circ}$  after crystallisation from dilute methyl alcohol. It closely resembles methyl diketoapocamphorate, and gives a strong red coloration with alcoholic ferric chloride; it is soluble in aqueous sodium hydrogen carbonate (Found: C = 56.20; H = 6.52.  $C_{12}H_{16}O_6$  requires C = 56.26; H = 6.30 per cent.).

The quinoxaline derivative, although evidently formed, as shown by the green fluorescence of the alcoholic solution, when the diketonic ester was treated with *o*-phenylenediamine, could not be isolated in a pure condition.

The semicarbazone, after crystallisation from alcohol, in which it is easily soluble, melts at  $177^{\circ}$  with decomposition.

The diketonic ester was hydrolysed by boiling for two hours with an excess of 20 per cent. sulphuric acid, and the diketone formed was isolated by distillation in steam. The distillate was saturated with ammonium sulphate and extracted with ether. On removing the ether, the diketone was obtained as a pale yellow oil which immediately solidified on cooling.

*1-Methyl-1-ethylcyclopentane-3:4-dione* crystallises from light petroleum in slender, colourless needles melting at  $63^{\circ}$ ; its alcoholic solution gives an intense port-wine coloration with aqueous ferric

chloride. It is soluble in sodium hydrogen carbonate solution (Found: C = 68.89; H = 8.78.  $C_6H_{12}O_2$  requires C = 68.53; H = 8.64 per cent.). A solid quinoxaline derivative could not be prepared.

The *disemicarbazone*, prepared in the usual way, was purified by boiling with a large volume of alcohol, in which it is only very slightly soluble. It is a microcrystalline powder, melting with decomposition at  $240^\circ$  (Found: C = 46.90; H = 7.19.  $C_{10}H_{18}O_2N_6$  requires C = 47.22; H = 7.16 per cent.).

The residue remaining in the flask after the hydrolysis of the diketonic ester deposited 4 grams of crude  $\beta$ -methyl- $\beta$ -ethylglutaric acid, which was identified in the usual way.

*Methyl  $\beta\beta$ -Diethylglutarate*.—This ester boils at  $131^\circ/16$  mm. (Found: C = 60.80; H = 9.28.  $C_{11}H_{20}O_4$  requires C = 61.05; H = 9.34 per cent.).

Fifteen grams of the ester were employed in each experiment. On adding the reaction-mixture to ice-cold, dilute sulphuric acid, a dark brown oil separated which did not solidify after several hours. The oil was therefore taken up in ether, the extract washed with water, dried, and evaporated, 11–15 grams of a dark brown oil remaining. This was distilled in steam, when 2–3 grams of a pale yellow oil, having a camphor-like odour, passed over. The oil gave an intense red coloration with ferric chloride, but it showed no sign of solidification and was therefore treated with semicarbazide. A small quantity of a very sparingly soluble semicarbazone was first precipitated, melting with vigorous decomposition at  $241^\circ$  after purification by extraction with hot alcohol. This was identical with the *disemicarbazone* described on page 1506. The mother-liquor was diluted, when another substance gradually separated. This was found to be readily soluble in hot alcohol, and crystallised in colourless, feathery crystals melting at  $166^\circ$  without decomposition. Analysis showed it to be the *semicarbazone* of *methyl 1:1-diethylcyclobutane-3-one-2-carboxylate* (II) (Found: C = 55.05; H = 8.11; N = 17.84.  $C_{11}H_{19}O_3N_3$  requires C = 54.75; H = 7.96; N = 17.42 per cent.).

The liquid which remained after steam-distillation was boiled for two hours with an excess of 20 per cent. sulphuric acid, and again distilled in steam. In this way 0.7 gram of a pale yellow oil was obtained. This oil was also enolic and on treatment with semicarbazide gave a small quantity of the *disemicarbazone*, melting at  $241^\circ$  described above.

The residue from the steam-distillation consisted of crude  $\beta\beta$ -diethylglutaric acid, which separated on cooling, and weighed 7–8 grams.

*Methyl cyclohexane-1:1-diacetate*.—This ester is a colourless liquid boiling at 164°/26 mm. (Found: C = 62.92; H = 8.88;  $C_{12}H_{20}O_4$  requires C = 63.11; H = 8.85 per cent.).

Nineteen grams of the ester were used for each condensation. It was not found possible to isolate a diketonic ester from the reaction mixture, which consisted almost entirely of *cyclohexane-1:1-diacetic acid*. The crude product, however, gave a coloration with alcoholic ferric chloride and therefore contained a little enolic substance, which was isolated by distillation in a current of steam. The distillate was saturated with ammonium sulphate and extracted with ether. After removal of the ether with the aid of a column, the residue weighed about 1 gram, and consisted of *cyclohexanespirocyclopentane-3:4-dione* (IV) (Kon, *loc. cit.*, p. 522) together with a trace of *cyclohexanespirocyclobutane-3-one* (III) (*ibid.*, p. 520), as shown by the formation of the corresponding semicarbazones. The presence of the diketone was further established by preparing the characteristic quinoxaline derivative with *o*-phenylenediamine. After crystallisation from dilute alcohol, this separated in buff-coloured needles melting at 99–100° and was proved to be identical with the quinoxaline derivative of *cyclohexanespirocyclopentane-3:4-dione* prepared by Kon (*loc. cit.*), by direct comparison with the original specimen.

The residue in the flask after steam-distillation deposited on cooling 14.5 grams of *cyclohexane-1:1-diacetic acid* (corresponding to 16.5 grams of ester used or 87 per cent.).

An alternative method which was also employed, was to extract the ethereal solution of the crude reaction product with sodium hydrogen carbonate solution. In this way, the acid together with some acid ester was recovered and the diketone remained in the ethereal solution.

An experiment carried out under precisely similar conditions, without the addition of methyl oxalate, gave the same products in comparable yield.

#### *Action of Potassium on Methyl $\beta\beta$ -Diethylglutarate.*

The procedure described in Part VII of this series (this vol., p. 518) was followed, using 65 grams of ester. The products were:  $\beta\beta$ -diethylglutaric acid and its acid ester, 8 grams; portion not extracted by sodium hydrogen carbonate solution, 43 grams (after removal of the xylene). On distillation under diminished pressure, the latter gave a large fraction (15 grams) boiling at 125–130°/18 mm., which was strongly enolic, giving an intense port-wine coloration with alcoholic ferric chloride. It was therefore treated with semicarbazide (12 grams) dissolved in sodium acetate solution.

The *disemicarbazone* of 1 : 1-diethylcyclopentane-3 : 4-dione,  $\text{C}_2\text{H}_5 > \text{C} \begin{cases} \text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \\ \text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \end{cases}$ , was obtained as a microcrystalline, white deposit after a few hours, and more was precipitated on dilution with water, the total yield being 7 to 8 grams. The disemicarbazone is best purified by boiling with alcohol, in which it is very sparingly soluble; after purification, it melts at  $241^\circ$  with vigorous decomposition (Found : C = 49.41; H = 7.84.  $\text{C}_{11}\text{H}_{20}\text{O}_2\text{N}_6$  requires C = 49.22; H = 7.53 per cent.). The diketone can be regenerated from the disemicarbazone by distillation with 10 per cent. aqueous sulphuric acid and forms a pale yellow oil boiling at  $245^\circ$ . It could not be induced to solidify and therefore was analysed without further purification (Found : C = 69.42; H = 9.23.  $\text{C}_9\text{H}_{14}\text{O}_2$  requires C = 70.08; H = 9.15 per cent.).

The acid liquid remaining after regeneration of the diketone deposited a solid which crystallised from alcohol in buff needles, melting at  $223^\circ$ . This was doubtless a triazine of the type obtained by Kon (*loc. cit.*, p. 522).

A very small amount of a soluble semicarbazone, melting at  $166^\circ$  after recrystallisation from alcohol, was slowly deposited after dilution of the mother-liquor, when the disemicarbazone had been completely precipitated. This was identical with the semicarbazone described on page 1504, showing that a minute quantity of methyl 1 : 1-diethylcyclobutane-3-one-2-carboxylate (II) was formed during this reaction.

In conclusion, our thanks are due to the Chemical Society for a grant which has partly defrayed the cost of the materials used in these experiments.

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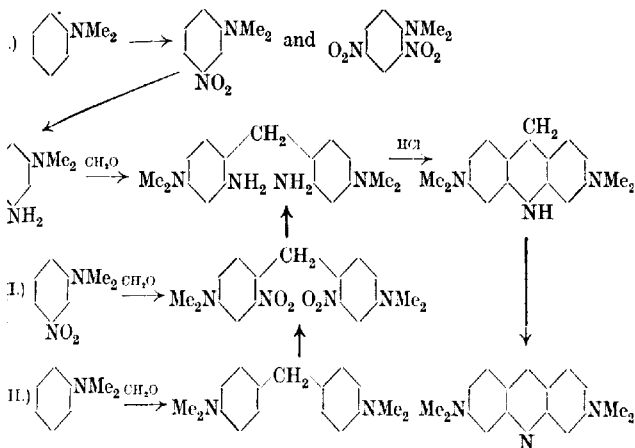
[Received, June 15th, 1922.]

## CLXXVII.—2 : 8-Tetramethyldiaminoacridine.

By KISHORI LAL MOUDGILL.

THE following experiments were undertaken with a view to prepare 2 : 8-tetramethyldiaminoacridine, using dimethylaniline as the starting material. For the preparation of the intermediate compound, 2 : 2'-diamino-4 : 4'-tetramethyldiaminodiphenylmethane, from dimethylaniline by nitration, reduction, and condensation with formaldehyde, three series of experiments were undertaken, each differing from the others in the order in which the above reactions were carried out. The scheme is outlined below. The

best results were obtained in the third series, which alone will be described.



#### EXPERIMENTAL.

*Nitration of 4:4'-Tetramethyldianodiphenylmethane.*—Ullmann and Marie used potassium nitrate in carrying out this nitration (*Ber.*, 1901, **34**, 4315). Attempts were made to substitute sodium nitrate, but without success. However, the following interesting method of preparing 3:3'-dinitro-4:4'-tetramethyldianodiphenylmethane was discovered.

A saturated solution of sodium nitrate (68 grams) in water (60 c.c.) was treated with 300 grams of concentrated sulphuric acid, and the mixture obtained was used to nitrate 100 grams of 4:4'-tetramethyldianodiphenylmethane dissolved in 200 grams of concentrated sulphuric acid, the reaction being controlled with the aid of a freezing mixture. On adding sodium hydroxide, a red compound was obtained. It was crystallised from glacial acetic acid, and melted at 124°, alone or mixed with 3:3'-dinitro-4:4'-tetramethyldianodiphenylmethane prepared by another method. The yield was 81 per cent. (Found: C = 59.0; H = 5.9.  $C_{17}H_{20}O_4N_4$  requires C = 59.2; H = 5.8 per cent.).

The required 2:2'-dinitro-4:4'-tetramethyldianodiphenylmethane was prepared by nitrating 4:4'-tetramethyldianodiphenylmethane with nitric acid (Pinnow, *Ber.*, 1899, **27**, 3162).

*Reduction of 2:2'-Dinitro-4:4'-tetramethyldianodiphenylmethane.*—All the commoner methods of reduction were tried. The



best results were obtained with tin and hydrochloric acid. The nitro-compound (10 grams) was dissolved by heating with 240 c.c. of dilute hydrochloric acid containing 75 c.c. of the concentrated acid. The solution was cooled, and tin added gradually, the temperature being kept below 60°. The reduction was completed on a boiling-water bath, the solubility in glacial acetic acid of the precipitate given by the reaction mixture with sodium hydroxide being taken as a criterion of complete reaction. The unchanged tin was filtered off, the tin in solution precipitated by hydrogen sulphide, and excess of sodium hydroxide added to the clear filtrate. A 42 per cent. yield of yellow leaflets, m. p. 142°, was obtained after crystallisation of the base from rectified spirit.

2 : 8-Tetramethyldiaminoacridine.—Ammonia was eliminated from the preceding compound by heating with dilute hydrochloric acid, and a dihydro-derivative of the above compound obtained. Boehringer (*J. pr. Chem.*, 1896, [ii], 54, 244) recommends the oxidation of the dihydro-compound either by passing air through the acid solution or by the addition of ferric chloride. Both these methods were tried and found unsatisfactory. After either of these treatments the acid solution was made alkaline with sodium hydroxide, and the orange precipitate dried. Attempts were made to crystallise it, but without success. Once or twice very small yields of light, yellow flakes were obtained, but generally a tarry oil was deposited on cooling a hot solution of the compound. The melting point of the substance was 174–176°. A sufficiently pure specimen for analysis could not be obtained.

The following method of isolating the acridine compound proved more successful. The acid solution was poured into water and solutions in water of zinc chloride (1 part) and ferric chloride (2 parts) were added. On standing, crystals of the zinc salt of the base separated out. These were filtered, redissolved in water, and excess of sodium hydroxide added, when the precipitated zinc hydroxide almost redissolved. The mixture was extracted with benzene and the base recovered. After recrystallisation from benzene it melted at 181° (Found: C = 77·6; H = 7·2.  $C_{17}H_{19}N_3$  requires C = 77·3; H = 7·1 per cent.).

A mixture of the two compounds, m. p. 174° and 181°, respectively, was found to melt at 130–141°. This points to the two compounds being different. They both give fluorescent solutions in alcohol or other solvent, and dissolve in hydrochloric acid with a deep red colour, which turns orange on dilution. So far, the compound melting at 174° has not been identified.

The author's thanks are due to Professor Sir William Pope,

F.R.S., by whom the investigation was suggested, and to Dr. C. S. Gibson for their help and guidance.

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### CLXXVIII.—*Brominated isoCyanines.*

By KISHORI LAL MOUDGILL.

THE *isocyanines* were discovered by Hoogewerff and van Dorp, and independently by Spalteholz, in 1883, but their use as sensitisers was first recognised by Miethe twenty years later (*Chem. Ind.*, 1903, 26, 54). Since then the firm of Meister, Lucius, & Brünig have put them on the market under the trade names of pinaverdol\* and pinacyanol,† for making panchromatic plates. Pinaverdol is synthesised by boiling an alcoholic solution of quinoline methiodide and quinaldine methiodide with sodium ethoxide; and pinacyanol by condensing quinaldine ethiodide (2 mols.) with formaldehyde with the aid of sodium ethoxide. The constitution of these compounds has been discussed by Mills and Wishart (*T.*, 1920, 117, 579) and by Otto Fischer (*J. pr. Chem.*, 1918, [ii], 98, 204).

The present work was undertaken with a view to study the modifications in sensitiveness brought about by the introduction of an atom of bromine in the benzene ring of the quinaldine nucleus of pinaverdol and pinacyanol. As is obvious, four isomerides, with bromine in the 5-, 6-, 7-, or 8-position, may be obtained. Of these the 6- and 8-bromoquinaldines may be prepared by condensing *p*-bromoaniline and *o*-bromoaniline, respectively, with acetaldehyde. When condensations are made with acetaldehyde and *m*-bromoaniline, two bromoquinaldines may evidently be obtained, the bromine atom in the meta-position with respect to the amino-group in the primary base occupying the 5- or the 7-position in the bromoquinaldine.

6-Bromoquinaldine has been prepared by Batrow and MacCullum, but they omit to give their yields (*J. Amer. Chem. Soc.*, 1904, 26, 704). Since preparation by their method gave poor yields, it was modified, and relatively larger yields were obtained. Of the two isomerides to which *m*-bromoaniline may give rise on condensation with acetaldehyde, only one has been isolated. The position of the bromine atom has been left undetermined for the present.

\* 1 : 1'-Dimethylisocyanine iodide.

† 1 : 1'-Diethylazurine iodide.

It is believed that, on account of steric hindrance, 8-bromoquinaldine would not give its alkyl iodide readily; moreover, 8-substituted quinaldines give a very small yield of the sensitiser (D.R.-P. 167159, 167770; Hamer, T., 1921, 119, 1432). Therefore no attempt has been made to prepare the dyes from this compound.

The relative sensitising effect of the different dyes was ascertained by photographing at the ordinary temperature the spectrum of a point of light on a "rapid" plate which had been immersed in a solution of one part of the sensitiser in 75,000 parts of 35 per cent. alcohol.

#### EXPERIMENTAL.

**6-Bromo-1:1'-dimethylisocyanine Iodide.**—To a mixture of 11.7 grams of 6-bromoquinaldine methiodide and 17.4 grams of quinoline methiodide dissolved in 300 c.c. of boiling absolute alcohol a hot solution of 0.83 gram of sodium in absolute alcohol was added. The mixture having been boiled for fifteen minutes, 1 c.c. of glacial acetic acid was added to the product, and on the next day the solid which had been deposited was collected and extracted with methyl alcohol, 100 c.c. at a time, until the residue showed a metallic lustre. This was recrystallised twice from methyl alcohol. Only 0.1 gram of green crystals was obtained.

This method of preparation was tried five times, with slight modifications, but only mere traces of the compound could be obtained. An analysis could not be attempted, but the spectrograph indicated that the compound possessed sensitising properties.

Another method was tried. Equal weights of the two methiodides were heated together in ten times their weight of pyridine for eight hours, when a crimson solution was obtained, which, on cooling, deposited golden-brown needles, very sparingly soluble in common organic solvents. The compound may be an "apocyanine."

**6:6'-Dibromo-1:1'-diethylazurine Iodide.**—To 9.5 grams of quinoline ethiodide and 12.6 grams of 6-bromoquinaldine ethiodide dissolved in 300 c.c. of boiling rectified spirit, 7 c.c. of formaldehyde solution containing 38 grams per 100 c.c. were rapidly added, followed by a hot solution of 0.92 gram of sodium in 50 c.c. of rectified spirit. The mixture was boiled for fifteen minutes, and the solid that separated was filtered from the red mother-liquor after twelve hours, and extracted with rectified spirit, 100 c.c. at a time, until the extract was coloured blue. An attempt was made to crystallise the solid from methyl alcohol, but it was too sparingly soluble, and in order to obtain the pure product the solid was extracted with methyl alcohol in a Soxhlet apparatus

during six weeks, when 1.1 grams of green crystals were obtained (Found: in material dried at  $140^{\circ}$ ,  $\text{AgI} + \text{AgBr} = 95.8$ .  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{Br}_2\text{I}$  requires  $\text{AgI} + \text{AgBr} = 95.5$  per cent.).

5:5'(or 7:7')-Dibromo-1:1'-diethylazurine Iodide.—The pinacyanol derived from the bromoquinaldine obtained from *m*-bromoaniline was prepared in the same way as 6:6'-dibromo-1:1'-diethylazurine iodide. The green compound that separated from the reaction mixture was recrystallised from methyl alcohol without its having to be extracted from any red impurity. It was found to be more soluble than its isomeride (Found:  $\text{AgI} + \text{AgBr} = 95.6$ .  $\text{C}_{25}\text{H}_{25}\text{N}_2\text{Br}_2\text{I}$  requires  $\text{AgI} + \text{AgBr} = 95.5$  per cent.).

#### Conclusions.

(a) Comparison by the photographic method of pinacyanol and its 6:6'- and 5:5'(or 7:7')-dibromo-derivatives shows that the introduction of the halogen has considerably depressed the sensitiveness.

(b) There has been a shift of sensitiveness towards the red end of the spectrum (compare Hamer, *loc. cit.*).

The investigation was suggested by Dr. W. H. Mills, whom I wish to thank for constant help and guidance. My thanks are also due to Sir William Pope for permission to publish the results.

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### CLXXIX.—*The Viscosity of Cellulose in Cuprammonium Hydroxide Solution. Part I. The Determination of the Viscosity.*

By REGINALD ARTHUR JOYNER

IN all technical work connected with cellulose an accurate determination of its viscosity in cuprammonium hydroxide (Schweitzer's reagent) is of importance, for it is largely the viscosity of the cellulose which determines the viscosity figure of solutions of the nitrocellulose or acetylcellulose made therefrom. If, for example, a nitrocellulose is required which will dissolve in acetone to give a high viscosity, a cellulose must be taken which will give a high viscosity in Schweitzer's reagent.

The determination of the viscosity of cellulose presents several difficulties, the chief one being due to the rapid action of oxygen on the solution, resulting in a lowering of the viscosity. These

difficulties were recognised by Gibson, Spencer, and McCall (T., 1920, 117, 484) and a method was developed of dissolving the cellulose in the reagent so that the effect of the oxygen could only be a small one, whilst their method of using the falling-sphere viscometer greatly simplified the actual determination of the viscosity. As, however, widely varying results were sometimes obtained with one and the same cotton by the above method, the whole question of the viscosity of the cellulose in cuprammonium hydroxide was re-investigated. A modification in making up the cellulose solutions was developed, a different method for the preparation of the Schweitzer reagent being used, and the effect on the viscosity of varying the concentration of the cellulose, the copper, and the ammonia was investigated. The cellulose used in this work was cotton sliver which had been kiered with 3 per cent. sodium hydroxide for a length of time depending on the viscosity required. The viscosity throughout is given in seconds for a fall of a 1/16" diameter steel ball through 15 cm. of a solution in a tube of 1.0 cm. diameter at a temperature of 20°. To obtain the absolute viscosity, the time in seconds is multiplied by 0.52.

*Method for the Preparation of the Cuprammonium Solutions.*

The method adopted for the preparation of the cuprammonium solutions was not that used in the above-mentioned paper, but the solutions were simply made by bubbling air through a mixture of copper turnings and strong ammonia. This procedure requires no attention, and concentrated solutions containing more than 30 grams of copper per litre can be obtained. The copper must be clean, and it was found that the addition of a small amount of sucrose, about 1 gram per litre, hastened the dissolution of the copper.

The effect of the addition of substances such as sucrose on cuprammonium hydroxide has been investigated by W. Traube (Ber., 1921, 54, [B], 3220). He found that a solution of ammonia saturated with copper hydroxide took up more copper hydroxide on the addition of glycerol, sucrose, etc. The concentration of sucrose used here was only about 1/50th that used by Traube, and the extra copper dissolved owing to combination with sugar would not be available in dissolving cellulose. It seemed probable that with sucrose the copper remained cleaner than without it, and therefore permitted the reaction to go forward. It was found that after standing for four weeks, a solution containing 25.6 grams of copper with a little sucrose was unaltered, whilst the copper content of the one without sucrose fell to 20 grams per litre. A solution containing 36 grams of copper per litre remained unaltered for three

weeks, and owing to its high copper content dissolved as much as 90 grams of cellulose per litre. The estimation of the copper in these solutions is simply carried out by evaporating a definite volume to dryness and weighing the copper oxide left. The ammonia is estimated in the usual way, and then the solution can be made up to the desired concentration of copper and ammonia.

The cuprammonium solution made by the above method contains a certain amount of nitrite. The best way of estimating this nitrite was to add the solution slowly to a definite volume of standard permanganate, strongly acidified, until the colour of the permanganate disappeared. By the above method it was found that the amount of nitrite in a freshly prepared solution was about 1 gram per litre calculated as nitrous acid. Solutions of cuprammonium hydroxide combine slowly with oxygen on standing, whilst when shaken with oxygen the reaction is much faster. With a solution containing 13 grams of copper per litre the amount of nitrite ultimately found was 4.4 grams calculated as nitrous acid, whilst the concentration of nitrite rose to 10 grams per litre with a solution containing a high concentration of copper.

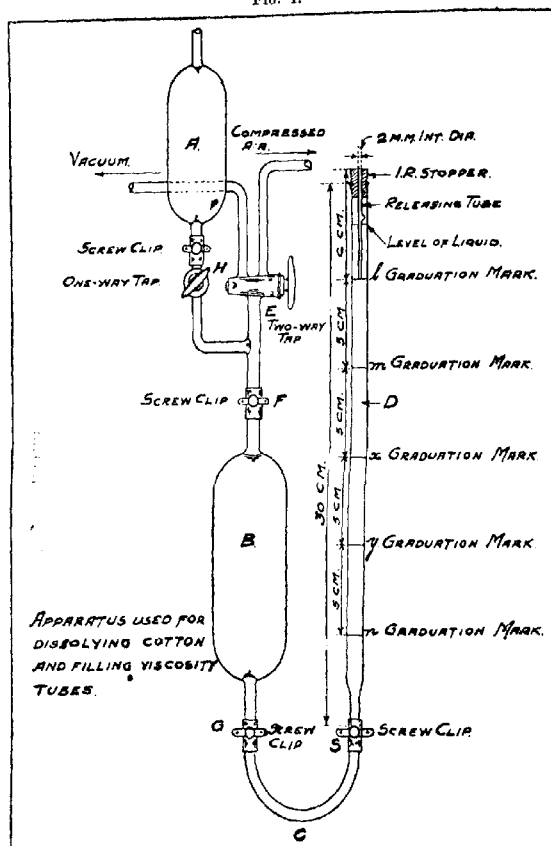
It was found that cuprammonium solutions made by the above method gave practically the same viscosities with cottons of widely varying viscosities as the solutions made by dissolving well-washed copper hydroxide in ammonia.

*Method of Dissolving the Cellulose and Filling the Viscosity Tubes.*

Viscosity measurements of low or medium viscosity cottons, by the method developed by Gibson, Spencer, and McCall, give satisfactory results, but solutions of high viscosity cottons gave trouble, especially in the filling of the viscosity tubes. At the same time their method has obvious disadvantages, for air has to be admitted to the solution before the viscosity is determined, and on inverting the bottle the air passes through the solution. This has two disadvantages. Some of the air obviously must react with the cotton, and when the solution is very viscous it is not easy to get the solution into the tubes free from bubbles. These bubbles gradually move up the viscosity tube, and on many occasions it was evident that part of the solution through which the bubble had travelled was less viscous than the other part. The method of making up the solutions and the filling of the tubes were therefore modified in the following manner. Instead of using an ordinary bottle for making up the solution, a glass tube (B, Fig. 1), 10 cm. long and 5 cm. wide, drawn out at each end to a narrow tube 0.7 cm. wide and 3 cm. long, is used. The correct weight of cotton

is pushed down one of the ends into the bottle, pieces of rubber tubing about 6 cm. long, with screw clips, are slipped over the end tubes, and the bottle is attached by one of the rubber tubes to the filling apparatus. This consists of a two-way tap, *E*, which allows

FIG. 1.



the bottle *B* to be connected either with the vacuum or with a supply of compressed air or any other gas. Between this tap and the screw clip *F* there is a side tube connecting with *A*, the reservoir for the cuprammonium solution, which is closed by a single-way tap, *H*.

In making up a solution, the vessel *B* which contains the cotton is connected with the filling apparatus, the screw clip being shut. *B* is evacuated and *E* is turned off, so that by opening *H* the solution in *A* is allowed to enter *B*. *H* is closed and *E* opened and shut three times to get all the air out of the cotton. The screw clip *F* is shut and the vessel *B* is disconnected and well shaken until solution is complete. It is then kept under water in an upright position. In filling the viscosity tube *D*, *B* is connected as before with *E* and also with *D*, by means of the glass tube *C* and rubber tubing. The tap *E* is opened and air or any other gas is allowed to flow in and then, on opening *G* and *S* and applying a slight pressure, the tube is easily filled. Several tubes may be filled from the same bottle, if necessary. With this arrangement the time taken for making up a solution is very little more than with the old method, but the filling of the viscosity tubes is quicker, easier, and is free from any objection. The viscosity tubes, being open at both ends, are easier to clean and dry than those closed at the lower end.

Cotton sliver which had been boiled with normal sodium hydroxide for four hours was dissolved in a cuprammonium solution containing 11.8 grams of copper and 192 grams of ammonia per litre, according to the Gibson, Spencer, and McCall method and to the above method. At the same time samples of the sliver were placed under water in an evacuated vessel in order to free them thoroughly from air, then as much as possible of the water was squeezed out, thus leaving about the same weight of water as of cotton. These air-free celluloses were dissolved according to the new method. The dilution caused by the water in the cellulose would be therefore about 2 per cent. and hence by taking a correspondingly less amount of Schweitzer reagent the change in viscosity caused by diluting by this amount may be neglected. The solutions were made up in triplicate, and two tubes were filled from each bottle.

The results were as follow :—

TABLE I.

*Comparison of the viscosity in seconds of a cotton as determined by the three methods, by the fall of a 1/16 in. steel ball through 15 cm.*

Two grams of cellulose in 100 c.c. of solvent.

G. S. and M.'s method.	New method.	New method with air-free cotton.
3240	4230	4020
3180	4050	3900
3735	4035	4065
3600	3975*	3975
3600	4050	4035
—	—	3975



It is observed that there is an increase of about 12 per cent. on the viscosity of the solution made up by the new method, and that freeing the air from the cellulose beforehand makes no difference.

It will be seen that in the duplicate determinations the viscosity of the solution in the second tube is 1 to 2 per cent. less than that of the solution in the first tube. In blowing out the solution no great care was taken, and mixing of the air and the solution may have taken place. As in the above determinations air was employed to drive the solutions into the viscosity tubes, an experiment was carried out to see whether the presence of air affected the results. One hundred and fifty c.c. of solution were made up and successive tubes were carefully filled at intervals of two minutes until the bottle was empty, and the time of fall was taken for each 5 cm. of the tubes. The viscosity of the solutions in each tube is generally given by the time of the fall for the last three 5 cm. distances.

TABLE II.

*Effect of air-blowing on the viscosity.*

Tube No.	Time of exposure in min.	Viscosity in sec. for each 5 cm. of tube.				Viscosity for last 15 cm.
		1st.	2nd.	3rd.	4th.	
1	0	1230	1215	1215	1234	3664
2	2	1215	1230	1215	1215	3660
3	4	1185	1260	1260	1230	3750
4	6	1260	1230	1200	1215	3645
5	8	1080	510	165	90	765

This shows that the air effect is confined to the top layer of the solution in the bottle and that therefore it is permissible to expel the solution by means of air.

When cellulose solutions were made up as above, they did not alter in viscosity by more than 2 per cent. after being kept for eight days under water and in the dark.

It was found eventually that the cause of great variations in the value of the viscosity of a particular batch of cotton was due to the difficulty in taking a representative sample. It was found necessary to pick over and open out every piece of cotton in a sample and then to mix them thoroughly.

*Effect of Dissolved Substances on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.*

The effect of dissolving sucrose, sodium chloride, and sodium sulphate in the cuprammonium hydroxide solution before adding the cellulose was investigated, and the results are given in Table III.

TABLE III.

*The effect of the addition of sucrose, sodium chloride, and sodium sulphate on the viscosity of a cellulose. Concentration of cellulose 2 grams per 100 c.c. of solvent.*

Grams of material added per litre.	0	5	10	17	20	40	50	80
Viscosity when addition was :								
Sucrose .....	240	235	395	—	488	—	Cell.	—
	225						insol.	
	240							
	245							
Sodium chloride .....	„	—	252	350	Cell.	—	—	—
			248	366	insol.			
Sodium sulphate .....	„	—	240	—	228	485	—	Cell.
								insol.

It will be seen that the addition of small amounts of the above substances has little or no effect on the viscosity, whilst the addition of larger amounts raises the viscosity and then renders the cellulose insoluble in the solvent. The effect of the addition of much sucrose is similar to that found by Traube (*loc. cit.*). He attributed the action to the sucrose combining with the copper and rendering it unavailable for the solution of the cellulose. The gradual increase in viscosity with smaller concentrations of sucrose confirms this.

The effect brought about by the addition of the salts cannot be due to this cause. It may be due to a salting-out action, similar to the effect of salts on soap solution.

*The Effect of the Concentration of Copper on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.*

In carrying out these experiments a well mixed cellulose was used, allowance always being made for the moisture content. The amount of ammonia in the reagent was always 210 grams per litre. The effect on the viscosity of the cellulose concentration was determined, and also the effect of diluting a cellulose cuprammonium hydroxide solution both with ammonia containing 210 grams per litre and with water. The results are given in Tables IV, V, VI, and VII, whilst the relationship between the copper content of cuprammonium hydroxide solutions and their absolute viscosity as found by the Ostwald viscometer is shown in Table VIII.

The results of Table IV are shown graphically on Fig. 2. The curves *aa'*, *bb'*, *cc'*, *cc'*, and *ff'* show the relation between the concentration of copper, in grams per litre, and the logarithm of the viscosity of solutions which contained quantities of cellulose varying from 0.5 gram to 3.0 grams per 100 c.c. of solvent. These curves are all of a hyperbolic nature, which shows that there is a limit to the effect produced by the concentration of the copper which lies in the neighbourhood of 30 grams per litre.

TABLE IV.

*Effect of varying the concentration of copper on the viscosity of cellulose in 100 c.c. of cuprammonium hydroxide solution.*

*Ammonia 210 grams per litre.*

Copper concentration. Grams per litre.	Grams of cellulose per 100 c.c. of solvent.					
	0.5	1.0	1.5	2.0	2.5	3.0
29.4		5.5		103	330	900
25	0.9		29.4			
24				113,110		
22.8					373	
20.0						1310
18				159,154	530	
16				180,182		2160
15				198,190		
14					980	3300
13		6.6		240,238		
12					*1500	
11.8						
11.5				316,310		
10.5				396,408		
10			59.4	505,517		
9	1.0					
8.5			90			
8.0		11.0	76.75			
7.0		*11.4				
6.0	1.1	*8.9				

\* Solution incomplete.

FIG. 2.

*Showing relation between concentrations of copper (grams per litre) and cellulose (grams per 100 c.c. solvent) and the log viscosities obtained.*

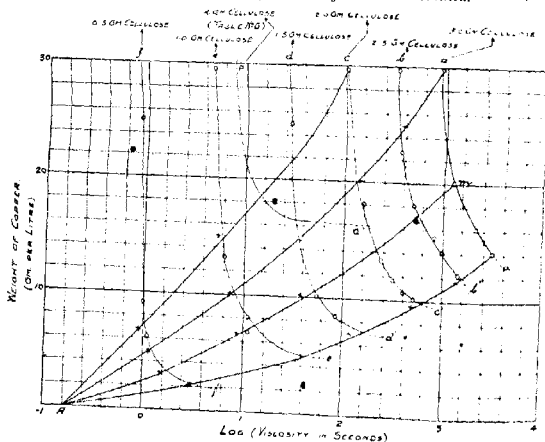


TABLE V.

*Effect of dilution by ammonia on the viscosity of cellulose cuprammonium hydroxide solutions, the ammonia content being constant at 210 grams per litre.*

Copper concentration.		Grams of cellulose per 100 c.c. of solvent.					
At start.	After dilution.	0.5	1.0	1.5	2.0	2.5	3.0
30	—	Viscosity (sec.).					
29.4	—	103					
—	25.0	330					
—	22.0	28.0					
20.0	20.0	138					
—	16.7	570					
—	15.0	5.4					
14.0	—	36					
—	13.3	205					
—	11.7	1500					
—	10.0	7.6					
—	9.3	37					
—	7.0	480					
—	6.7	0.9					
—	5.0	8.5					
—	4.7	1.1					
—	3.3	36					
—	2.3	1.5					
—	—	3.0					

TABLE VI.

*Effect of concentration of copper on the viscosity of a solution of cellulose of less viscosity than that used in previous tables. Concentration of cellulose 4 grams per 100 c.c. of solvent.*

*Ammonia 210 grams per litre.*

Copper concentration.	Viscosity in sec.
29.4	7.9
22.8	10.5
18.0	15.2
16.0	38.0*

\* Solution incomplete.

TABLE VII.

*Effect of the concentration of copper on the absolute viscosity of ammonia solution containing 220 grams of ammonia per litre.*

Concentration of copper.		Viscosity in C.G.S. units.	Log. viscosity.
Grams per litre.	Density.		
30.1	0.9560	0.0165	-1.7825
8.0	0.9293	0.0144	-1.8420
0	0.912	0.0136	-1.8665

With low copper concentration the tendency is for the solutions to have an infinite viscosity, but this is not realised since the cotton

will not dissolve completely in these weak solutions, and the logarithms of the viscosities of the heterogeneous mixtures obtained in these cases obviously do not lie on the respective curves.

On diluting a concentrated cellulose cuprammonium hydroxide solution with ammonia solution such that the concentration of cellulose coincided successively with those for the curves  $aa'$ ,  $bb'$  . . .  $ff'$ , it was found that the logarithms of the viscosities, on being determined, lay on these curves. This showed that equilibrium was established at these points, the same result being obtained whether the solution was prepared by directly dissolving cellulose or by diluting a concentrated solution with ammonia. On connecting the points obtained in this way, the curves  $Aa'$ ,  $Am$ ,  $Aa$ , and  $Ac$  (Fig. 2) were obtained. It was found that it was thus possible to obtain cellulose solutions which could not be made directly with very low concentrations of copper, owing to the inability to dissolve the cotton. The latter, however, was not precipitated by dilution of the solution with ammonia. The curves were observed to meet at a point  $A$ , which represents the logarithm of the viscosity of a solution of ammonia as determined by the falling-sphere method, and this point is not very different from that obtained with cuprammonium hydroxide. The lowest of the transverse lines,  $Aa'$ , represents the viscosities of a saturated solution of cotton in the cuprammonium hydroxide solutions containing copper concentrations represented by the curve, and an ammonia concentration of 210 grams per litre.

It will be seen that the minimum copper concentrations for complete solution of a cellulose are almost proportional to the amount of cellulose present, and that about 2.3 grams of cellulose requires about 1 gram of copper. This means that 162 grams of cellulose, that is, one  $C_6H_{10}O_5$  group, requires 70 grams of copper, or about 1 gram-atom. On increasing the ratio of copper to cellulose in solution to three times this value, the least viscous solution is formed.

The effect of a low viscosity cellulose is shown by curve  $PQ$  (Fig. 2). The concentration of cellulose is 40 grams per litre, but for high concentrations of copper the curve almost coincides with that of a 10 grams per litre solution of high viscosity cellulose. On reducing the copper concentration with this low viscosity cellulose, the values for the viscosity rapidly increase until separation of cellulose takes place at a copper concentration of 16 grams per litre. This is the approximate value, as extrapolated from the curves for the high viscosity cotton, for the limit of copper concentration, and therefore it suggests that the solubility of a cotton in a cuprammonium hydroxide solution is dependent only on the copper

concentration, provided that there is enough ammonia present, and is independent of the viscosity of the cellulose.

*Effect of the Concentration of Ammonia on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.*

The effect of altering the ammonia content from 60 grams to 250 grams per litre was studied with different concentrations of cotton, using a copper concentration of 13.5 grams per litre. The results are given in Tables VIII, IX, and X.

TABLE VIII.

*Showing the effect of varying the concentration of the ammonia on the viscosities of cellulose cuprammonium hydroxide solutions containing 12.5 grams of copper per litre.*

Grams of cellulose per 100 c.c.	Grams of ammonia per litre.	Viscosity.	Log. viscosity.
2.0	254	720	2.86
	216	1020	3.01
	184	1500	3.18
	144	2070	3.32
	106	3240	3.51
	58	4980	3.70
1.0	254	16.5	1.22
	184	35	1.54
	106	79	1.90
	58	138	2.14
0.6	252	2.3	0.362
	215	3.2	0.505
	144	4.8	0.681
	62	4.3	0.919

Table IX shows the influence of an increase in the copper concentration of the solution.

TABLE IX.

*Effect of varying the concentration of ammonia on the viscosities of cellulose cuprammonium hydroxide solutions containing 24 grams of copper per litre.*

Grams of ammonia per litre.	2.0 Grams of cellulose per 100 c.c. of solvent.	
	Sec.	Log. viscosity.
235	576	2.76
177	937	2.97
92	2340	3.37

The results of experiments on a cotton having a lower viscosity than that used above are given in Table X.

TABLE X.

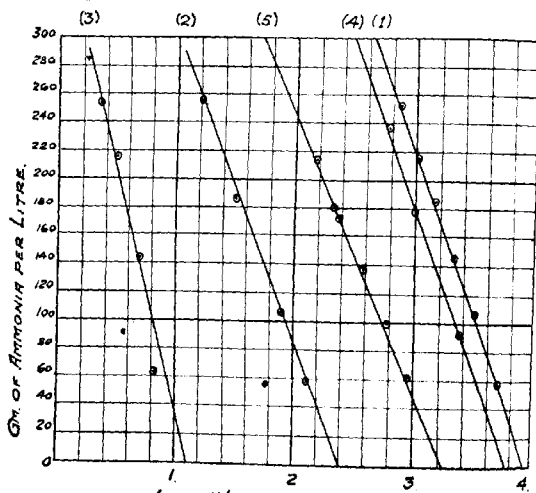
*Effect of using 2.0 grams of a cellulose of lower viscosity than that employed in Tables VIII and IX. Copper concentration = 13.5 grams per litre.*

Grams of ammonia per litre.	Viscosity. Sec.	Log. viscosity.
212	153.2	2.18
180	220	2.34
170	238	2.38
135	392	2.59
99.2	534	2.77
60.5	870	2.94

The curves obtained from Tables VIII, IX, and X, by plotting ammonia concentration against the logarithm of the viscosity, are shown in Fig. 3, and it will be seen that they form a series of straight

FIG. 3.

*Showing the effect of varying the concentration of ammonia on the viscosities of cellulose cuprammonium solutions containing 13.5 grams and 24.0 grams of copper per litre.*



- (1) 2.0 Grams of cellulose per 100 c.c. of solvent and 13.5 grams of copper.  
 (2) 1.0 " " " " " "  
 (3) 0.6 " " " " " "  
 (4) 2.0 " " " " " "  
 (5) 2.0 " " " " " "
- 24.0 "  
 (low viscosity) "  
 13.5 grams of copper

lines which are all practically parallel, with the exception of curve No. 3, which represents the effect for a very dilute cellulose, namely, 0.6 gram per 100 c.c. From the other curves it is seen that the decrease in the logarithm of the viscosity is directly proportional to the increase of ammonia concentration, and is independent of the viscosity either of the cotton, the amount taken, or the amount of copper in solution. The mean of the results shows that an increase in ammonia concentration of 10 grams per litre decreases the logarithm of the viscosity of the cotton by 0.047. Therefore from the values obtained with solutions containing 1 gram or more of cellulose in 100 c.c. of cuprammonium hydroxide solution of a definite ammonia content, the viscosity for any other ammonia concentration may be calculated.

*Effect of Cellulose Concentration on the Viscosity of Cellulose  
Cuprammonium Hydroxide Solutions.*

The effect on the viscosity produced by varying the concentration of the cellulose in solution was determined and it was found that when the logarithm of the viscosity was plotted against the concentration the curve obtained was nearly straight. Accordingly the relationship is best expressed by the Arrhenius formula, which states that

$\log \eta = \theta C$ , where  $\eta$  is the ratio viscosity solution/viscosity solvent,  $C$  is the concentration, expressed most accurately as grams of solute per 100 grams of solvent, and  $\theta$  is a constant depending on the nature of the cellulose used and is equal to

$$[\log (\text{viscosity of solution}) - \log (\text{viscosity of solvent})]/C.$$

The viscosity of the solvent cannot be found by the falling-sphere method directly, owing to the rate of fall being so great, but by plotting the logarithm of the viscosity of various cellulose solutions against the concentration a series of lines is obtained which meet at a point on the concentration axis giving a value of about -0.8, similar to the point A on Fig. 2. This gives for the viscosity of the solvent a value of about 0.160 sec. or 0.08 C.G.S. unit. The value found, using the Ostwald viscometer, is 0.015 C.G.S. unit. It would be probably incorrect to use the Arrhenius formula for extrapolating the value for the viscosity of the solvent, but in this case the number obtained gives a constant for  $\theta$  over considerable differences in concentration and great differences in viscosity. The value -0.8 is accordingly used in determining the value of  $\theta$ . It is seen that several factors affect the viscosity, for example, the concentration of the copper; as more cellulose is dissolved, more copper is removed from a state of true solution,



and, as shown in Fig. 2, a diminution in the uncombined copper results in increased viscosity of the solution and therefore in an increase in  $\theta$ . Another factor which may affect the viscosity is hydration of the sol, which may be altered by the concentration of the cellulose.

TABLE XII.

*The relationship between the log. viscosity of cellulose solution and its concentration.*

*Concentration of copper in 1 and 2 = 12 grams per litre.*

“ “ “ “ 3 “ 4 = 18 “ “ “

“ “ “ “ “ 5 = 29 “ “ “

$C$  = wt. of cellulose per 100 c.c. of solvent.  $\eta$  = viscosity in seconds.

Solution 1.				Solution 2.			
$C$ .	$\eta$ .	$\text{Log } \eta$ .	$\theta$ .	$C$ .	$\eta$ .	$\text{Log } \eta$ .	$\theta$ .
1.0	2	0.30	1.08	0.50	2.0	0.30	2.16
1.5	8	0.90	1.12	1.00	34.5	1.54	2.32
2.0	26	1.41	1.09	1.60	324	2.52	1.94
2.5	103	2.01	1.12	2.00	1580	3.20	1.99
3.0	540	2.73	1.17	2.40	6000	3.78	1.90

Solution 3.				Solution 4.			
$C$ .	$\eta$ .	$\text{Log } \eta$ .	$\theta$ .	$C$ .	$\eta$ .	$\text{Log } \eta$ .	$\theta$ .
1.0	1.7	0.23	1.01	2.00	1.2	0.08	0.43
1.5	5.5	0.74	1.01	2.00	5.4	0.73	0.50
1.75	11.0	1.04	1.03	5.00	54	1.73	0.50
2.0	16.8	1.22	1.00	6.00	285	2.45	0.55
2.25	30	1.48	1.09	7.00	Insol.		
2.5	46.5	1.67	0.98				
2.75	99	2.00	1.00				
3.0	192	2.28	1.02				
3.25	292	2.49	1.00				
3.5	402	2.60	0.97				

Solution 5.			
$C$ .	$\eta$ .	$\text{Log } \eta$ .	$\theta$ .
0.50	0.90	1.95	1.46
1.00	5.5	0.74	1.52
1.50	29	1.46	1.50
2.00	103	2.01	1.40
2.50	330	2.52	1.32
2.00	900	2.95	1.24

As regards the best copper concentrations for Schweitzer's reagent, it can be seen that any error in analysis causes the smallest change in viscosity when the concentration is high. It has been noticed, however, that with high copper concentrations, especially when the ammonia content is low, cellulose is gelatinised and then dissolves only slowly. The best concentration for general use is 13 grams of copper per litre with 20 grams of cellulose per litre, the ammonia concentration being 200 grams per litre. However, such a low concentration of cellulose does not differentiate between very low viscosity cottons, and for these a 4 per cent. solution of cellulose should be made in a Schweitzer reagent containing 20

grams of copper per litre, the ammonia concentration being the same as above. Using the Arrhenius formula, the viscosity for a 2 per cent. solution may then be calculated.

Occasionally even a 4 per cent. cellulose solution was not concentrated enough to bring out differences between very low viscosity celluloses, and a 9 per cent. solution of cellulose was made in a cuprammonium hydroxide solution containing 36 grams per litre. Thus, after a certain treatment, a cellulose gave a viscosity in seconds for a 4 per cent. solution of 4.7, whilst in a 9 per cent. solution the viscosity was 120. After further treatment the two viscosities were 2.5 and 30 respectively.

The above research work was carried out in 1920, and the author wishes to thank Messrs. Nobel Industries, Ltd., and Mr. Wm. Rintoul, O.B.E., F.I.C., for permission to publish this work. The author also wishes to thank Mr. J. J. Tidd, who carried out many of the experiments.

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[Received, May 12th, 1922.]

### CLXXX.—*The Sorption of Carbonyl Chloride by Beechwood Charcoal.*

By HUGH MILLS BUNBURY.

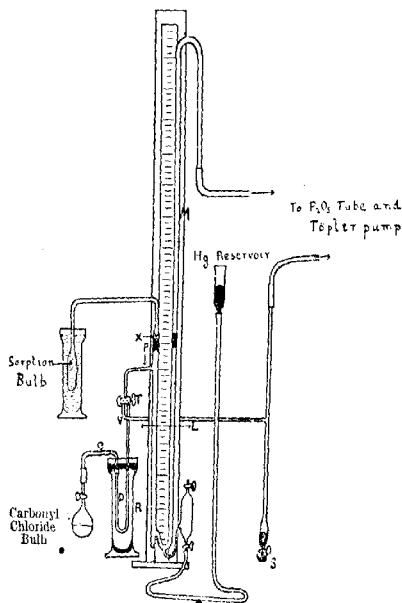
THE following is a brief description of some experiments which were undertaken with a view to ascertain to what extent carbonyl chloride is taken up and retained by charcoal, and the effect of time, temperature, and pressure on the sorption. No similar data are recorded in the literature of carbonyl chloride (compare the references compiled by Berolzheimer, *J. Ind. Eng. Chem.*, 1919, 11, 263). The results show that the sorption is affected by pressure and time in the usual way.

The apparatus employed was similar to that used by Travers *Proc. Roy. Soc.*, 1904, 74, 126; 1906, [A], 78, 9), and is shown in fig. 1.

The manometer, *M*, and the sorption bulb were exhausted by means of a Töpler pump, the mercury in both limbs being brought to the same level. The final level of the mercury was brought to a position indicated at *L*, by adjusting the mercury reservoir. The carbonyl chloride bulb was then weighed, and attached by means of stout pressure-tubing, which was securely wired on, to the capillary, *C*, which was connected with the capillary inlet tube, *D*. The rubber joints to the latter were submerged in a

mercury trough, *R*, to guard against leaks. The whole of the tubing from the tap on the carbonyl chloride bulb to the point *P* was filled with mercury, to exclude the possibility of the entry of air. The three-way tap, *T*, and the trap, *S*, were also fitted with mercury cup seals. All rubber-glass connexions were treated with glycerol before the joints were made. A thread of mercury was contained in both holes of the three-way tap and in the limb, *V*, of the side capillary leading to the pump. On opening the three-

FIG. 1.



way tap to both limbs, no movement of the mercury took place if the apparatus was quite air-tight. If even a slight movement occurred, the whole apparatus was re-exhausted and the joints made again. The tap on the carbonyl chloride bulb was then opened and carbonyl chloride allowed to enter the apparatus. The mercury in the manometer *M* instantly rose, but soon fell rapidly owing to the sorption of the gas in the charcoal. The carbonyl chloride bulb was quickly removed and re-weighed. When the sorption was complete, the level of the mercury was adjusted to the point

X, which was an inserted glass point just touching the surface of the mercury, and the height in the manometer read off by means of a telescope with micrometer eye-piece.

In the experiments on the rate of sorption, the mercury was kept at the glass point, X, by means of the reservoir, and the difference in height of the mercury in the manometer read off at definite intervals of time.

At first the carbonyl chloride attacked the mercury of the apparatus, but this was found to be due to free chlorine, which was present to the extent of 0.88 per cent. This free chlorine was removed by introducing mercury into the carbonyl chloride bulb before the experiment and allowing the gas and metal to remain in contact for some time at the temperature of a freezing mixture.

The charcoal used in this investigation was beech-wood carbon similar to that employed in gas masks.

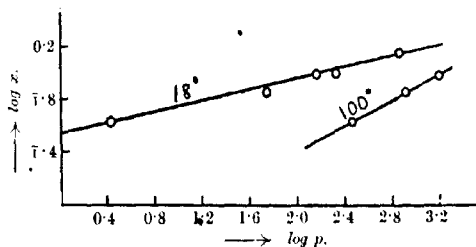
The apparatus was repeatedly exhausted at the end of each experiment, with the sorption bulb in the vapour of boiling sulphur. It was then flushed out with air several times and again exhausted at  $444^{\circ}$ .

The carbonyl chloride was estimated by drawing the gas through standard potassium hydroxide (approximately 0.2N) contained in a gas wash-bottle of spiral design. The contents of the bottle were then washed into a large beaker containing a few crystals of potassium iodide and some freshly prepared starch solution. The whole was acidified with a known volume of standard hydrochloric acid (approximately 0.5N) and the free iodine titrated with standard thiosulphate. Methyl-orange was then added and the solution neutralised with standard potassium hydroxide (approximately N). In working at temperatures below  $150^{\circ}$ , no free chlorine, or only a minute trace, was found.

#### Summary of Results.

The results are given in detail in Table I and plotted in Fig. 2.

FIG. 2.



The sorption of carbonyl chloride by charcoal.

They are apparently accurate to about 1 per cent. The points have been found to agree with the sorption formula  $x/m = kp^{1/2}$ .

Equilibria at 18° and 100° only have been investigated, since at temperatures above 150° the dissociation of carbonyl chloride into carbon monoxide and chlorine becomes appreciable. Thus at 150° it is 0.06 per cent., at 200° 0.4 per cent., at 300° 3.2 per cent., and at 400° 22 per cent.

TABLE I.

*The sorption of carbonyl chloride by 2.1922 grams of beech-wood charcoal.*

Temp.	Grams of COCl <sub>2</sub> .	Final pressure in mm.	Log $x$ .	Log $p$ .	$\frac{x}{m}$ .
14°	1.301	520	0.11420	2.71600	0.5935
18	1.385	730	0.14145	2.86332	0.6318
"	0.985	217	-1.99344	2.33646	0.4493
"	0.962	147	-1.98318	2.16732	0.4388
"	0.715	56	-1.85431	1.74819	0.3262
"	0.428	27	-1.63144	0.43136	0.1952
100	0.945	1596	-1.97544	3.20303	0.4310
"	0.693	825	-1.84073	2.91645	0.3161
"	0.420	292	-1.62325	2.46538	0.1916

At 18°,  $1/n = 0.231$ ;  $n = 4.33$ ;  $k = 0.235$ .

At 100°,  $1/n = 0.488$ ;  $n = 2.05$ ;  $k = 0.038$ .

The velocity of sorption is extremely rapid, almost all the gas represented by any particular equilibrium being sorbed within a few minutes: that is, equilibrium will be *practically* attained after a few minutes. However, the effect of more prolonged exposure is shown by the experiments in Table II.

TABLE II.

*The velocity of sorption of carbonyl chloride by charcoal at 14°.*

Carbonyl chloride introduced, 0.7434 gram.					
Time in minutes .....	6	8	10	12	18
Pressure in mm. of Hg. ....	160	115	100	94	91
Carbonyl chloride introduced, 0.3170 gram.					
Time in minutes .....	1	2	3	7	11
Pressure in mm. of Hg. ....	470	375	342	275	254

In conclusion, I wish to thank Professor McBain for advice and assistance.

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CLXXXI.—*The Composition of Paraffin Wax. Part II.*

By FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON.

No attempt has yet been made to effect a systematic fractionation of paraffin wax on the lines laid down by Sydney Young in his work on the lower-boiling members of the petroleum hydrocarbons.

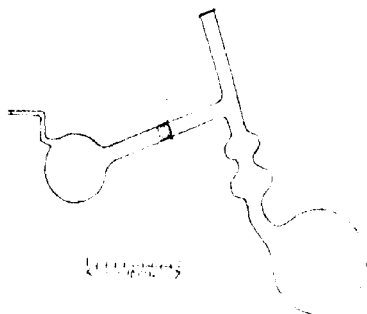
It has been assumed, however, since the work of Krafft in 1907—which will be discussed later—that paraffin was a complex mixture of a very large number of homologous members of the paraffin series of normal hydrocarbons.

During the investigation of the oxidation of this material, an account of which was published in this Journal (this vol., p. 512), it was found that a very partial fractionation gave fractions which showed a very marked difference in their rate of oxidation. This was considered to be a clear indication that a certain degree of separation had been effected, and it led directly to the attempt to effect a complete fractionation, an account of which forms the subject of this communication.

The material used was a part of that employed in the previous investigation, of Scotch origin, melting between 55° and 56°, showing a molecular weight of 366, an iodine value of 2.9, and  $d_4^{20}$  0.7628.

The apparatus employed for the fractionation was evolved after several preliminary trials and is sufficiently explained by reference to Fig. 1.

FIG. 1.



About 150 grams of wax was found to be a suitable quantity for a single distillation, and in all 950 grams of material were treated. As a source of heat a bunsen burner was found preferable to an

oil-bath; the fractionation had to be carried out very slowly, and "bumping" was minimised by the use of platinum tetrahedra. The vacuum required was obtained by the use of a Volmer mercury condensation pump, and no difficulty was experienced in maintaining the pressure between 0.12 mm. and 0.05 mm. during the period of the fractionation. The actual pressure was measured by means of a McLeod gauge, and the temperature by an ordinary small-bulb thermometer, calibrated at the National Physical Laboratory. Distilling under pressures in the neighbourhood of 0.1 mm., four fractions were collected at first, three between 170° and 230° and the residue boiling above the latter temperature. These were then divided into fractions boiling over a range of 10° and ultimately into those boiling over 5°. The total "boiling range" spread out with each fractionation, fractions being collected at temperatures as low as 125° and up to 280°.

Separation into large and small fractions was apparent at an early stage of the process, but it was not until the seventeenth fractionation that large amounts of material were obtained boiling over small ranges of temperature. This was markedly the case with the material boiling below 210°; above that temperature much greater difficulty was experienced in the operation.

At the end of the twenty-first fractionation it had become clear (see Table I) that the limit of the separation possible with the apparatus we were using had been reached.

The results of some of the fractionations are given in Table I; the earlier and middle have been omitted owing to lack of space.

Table II, column 3, gives details of the further fractionation of the smaller fractions boiling above 205°. This operation was carried out in a similar but smaller apparatus to that shown in Fig. 1.

During the entire distillation about 12 per cent. of the material was lost; considering the nature of paraffin wax, the experimental difficulties, and the very large number of separate fractionations, this may be regarded as a satisfactory result.

It is considered that about half of this loss could be traced to the residues left in the distillation flask at the end of a complete fractionation; and the rest to the fact that such residues at higher temperatures were dark in colour and were discarded as decomposition was suspected.

#### *Results of Fractionation.*

1. It is clear from the results of the last five fractionations (Table I) that the value  $\Delta W/\Delta T$  changes but little; small values tend to decrease and large ones to increase. It was judged that

TABLE I.  
Fractionation of Paraffin Wax. 1st to 16th, Press. = 0.3-0.5 mm. 17th to 21st, Press. = 0.05-0.12 mm.

Distillation.	5th.	6th.	13th.	14th.	15th.	16th.	17th.	18th.	19th.	20th.	21st.
Temp. range.	W.	W.	H.	H.	W.	H.	W.	H.	W.	H.	W.
150-155°	19	26.55	29.0	39.2	36.9	37.5	37.1	37.1	37.05	37.05	37.05
155-160°	27.0	31.45	50.2	33.9	43.9	55.3	77.2	14.2	63.2	76.6	76.3
160-165°	32.9	55.95	33.1	17.8	21.5	34.7	40.1	48.9	18.6	2.8	2.8
165-170°	37.1	58.0	37.1	40.9	69.5	51.8	93.9	66.1	109.3	133.4	130.0
170-175°	41.4	58.6	54.8	81.4	75.9	88.6	23.7	40.4	3.15	9.6	9.6
175-180°	87.0	69.85	64.3	75.4	46.0	21.3	16.8	8.1	43.15	8.6	NH
180-185°	56.5	109.35	50.4	7.6	8.4	127.9	168.4	31.0	30.8	24.6	4.9
185-190°	121.1	63.7	105.3	98.7	162.1	51.1	15.6	31.1	149.05	29.8	7.85
190-195°	58.0	86.45	66.2	70.6	36.0	93.1	15.9	8.1	23.25	4.7	13.1
195-200°	70.6	72.35	54.7	101.1	79.6	49.4	22.0	4.4	98.9	19.8	128.3
200-205°	104.8	126.75	70.9	16.2	83.6	42.8	16.3	16.2	38.2	7.6	36.35
205-210°	80.0	13.1	86.5	39.4	83.0	100.6	7.9	17.3	31.7	16.3	33.3
210-215°	136.6	25.9	61.1	20.2	44.3	21.3	3.5	28.1	9.1	9.2	10.7
215-220°	43.4	27.4	27.4	27.4	44.3	27.0	4.4	22.8	14.25	2.8	6.6
220-225°	47.2	14.41	15.9	22.0	18.6	33.3	6.7	17.7	13.4	5.6	5.6
225-230°	15.9	8.8	7.4	22.0	20.8	37.0	7.4	21.5	7.75	1.6	5.4
230-235°	33.15	33.15	14.1	29.1	35.0	8.45	0.28	38.0	33.3	6.6	See Table II.
240-245°	46.0	46.0	14.5	14.5	19.2	19.2	19.2	19.2	19.2	19.2	19.2
245-250°	45.260	45.260	14.5	14.5	19.2	19.2	19.2	19.2	19.2	19.2	19.2
250-260°	45.260	45.260	14.5	14.5	19.2	19.2	19.2	19.2	19.2	19.2	19.2

\* Redistilled in small flask.



TABLE II.

Fraction No.	Range of b. p. 0.1 mm.	Wt. in grams.	% of original paraffin.	Separate redistillation. Range of b. p. Press. mm.	Ref. letter.	Wt. in grams.	M. p.	Mol. wt. in benzene.	Density 100°/4°.	% Solubility in CHCl <sub>3</sub> at 15°.	Iodine value.
1	150-155°	37.05	3.9	140-150°	A	65.8	37.8°	291	0.7411	36.7	3.13
2	155-160°	76.30	8.0	150-151°	B		44.9°	325	0.7453	20.6	
3	160-165°	2.80	0.3								
4	165-170°	130.00	13.7	160-8 161.3°	C	121.8	51.9°	332	0.7501	8.38	2.45
5	170-175°	43.10	5.2	169-170°	D	40.0	53.2°	358	0.7523	5.42	
6	175-180°	7.85	0.8								
7	180-185°	163.13	17.2	180-182°	E	149.0	57.3°	394	0.7555	3.48	1.67
8	185-190°	5.05	0.5								
9	190-195°	178.95	17.7	190.5-191°	F	131.0	60.9°	419	0.7596	2.0	1.46
10	195-200°	9.20	1.0								
11	200-205°	65.20	6.8	196-198°	G	58	63.3°	449	0.7630	1.1	1.38
12	205-210°	21.70	2.3								
13	210-215°	9.75	1.0								
14	215-220°	32.00	3.4	217-219°	H	32	66.6°	434	0.7678	0.66	
15	220-225°	7.55	0.8								
16	225-230°	14.25	1.5								
17	230-235°	27.70	2.9								
18	235-240°	8.56	0.9								
19	240-245°	4.44	0.5								
20	245-250°	6.55	0.7								
21	over 250°	14.0	1.4	Synthetic dotriacontane.			69-72°	CS <sub>2</sub> solvent 528			
22				224.8°			70°	in benzene			
Total		836.7	88%					452	0.7645	0.4	1.76

a better separation could not be effected with the apparatus employed.

2. The data obtained from a redistillation of the large fractions from the twenty-first operation are given in Table II, and it will be seen that considerable amounts of material were obtained in no case boiling over a range of more than 2°.

3. Table II gives the amounts of the various fractions expressed as percentages of the original paraffin wax employed.

We consider that, making allowance for the loss on distillation, about 80 per cent. of this paraffin is composed of *seven substances of constant boiling point*. Of the remainder, 8 per cent. to 10 per cent. is composed of material boiling between 220° and 240° and probably containing *not more than two such substances*. The amount of wax boiling above 240° (press. 0.05 mm.) probably does not amount to more than 2 or 3 per cent.

4. These constant-boiling substances may be either fairly pure hydrocarbons or mixtures of hydrocarbons.

If the latter, they would, presumably, have melting points differing from those of their constituents. In Table II fractions lettered *A* to *H* show numbers for these constants which rise steadily with increase of boiling point: an indication that all the constituents belong to a general class of hydrocarbons. But that such constant-boiling substances may be mixtures has been clearly shown by S. Young, who found, for instance, that at 50° *cyclopentane* could not be separated from 2,2-dimethylbutane, that at 61–62° a mixture of the isomeric *isohexanes* distilled over, and at 70–71° a mixture of *n*-hexane and methylcyclopentane. The question as to the actual nature of these constant-boiling fractions can only be settled by chemical means.

It is difficult to compare this work with that of Krafft (*Ber.*, 1907, **40**, 4779), who investigated a Saxo-Thuringian wax obtained from lignite, fusing between 55° and 56°, and which he distilled in the vacuum of the "cathode rays," the exact pressure not being measured. After five fractionations he considered that he had isolated eighteen hydrocarbons, and an investigation of the residue indicated the presence of a further seventeen members, all of which were presumed to belong to the normal paraffin series. There can be little doubt, however, that five fractionations of such a complex mixture were entirely insufficient as a means of indicating the presence of constant-boiling substances.

Working with pressures certainly much higher than those used by Krafft, but with a still-head probably more efficient, we obtained little or no evidence of any definite separation until seventeen such operations had been carried out. We believe that Krafft

placed too much reliance on the small fractions he obtained, which in every case he regarded as corresponding with pure hydrocarbons. It will be seen from the fifth distillation, Table I, that it would have been possible to obtain a very large number of fractions of "constant boiling point," although all would have been small in amount.

It was only, however, when S. Young, between 1897 and 1905, investigated the fractionation of petroleum and devised the methods followed in this communication that it became possible to obtain some insight into the number of components present in such complicated mixtures. Krafft did not employ such criteria, and we have still to find out whether they are applicable to materials with high boiling points, distilled under very low pressures, and with a still-head very much less efficient than any of those used by Young.

In connexion with the extensive fractionations described in this communication, and the consequent period during which the vapour had been exposed to high temperatures, we must refer to the so-called "latent period" in the oxidation of the wax mentioned in the previous paper (*loc. cit.*, p. 499). It has been found that this period is decreased by heating the wax, and to an extent that depends on the temperature and the duration of the exposure. In a later paper we hope to be in a position to state what effect, if any, has been produced on this period by the fractionation.

During the operations we have observed no sign of "cracking," or of the evolution of any trace of gaseous material, but we have reason to suspect that a small amount of vapour derived from the original wax, and not greater than 0.5 per cent., passed through the pump.

The iodine values given in Table II clearly indicate that no unsaturated material had been formed during the fractionation.

#### *Physical Properties of the Constant-boiling Substances.*

1. In Table II the results are given of a separate distillation of the fractions obtained and described in Table I; the weight used, and that obtained over the given range of temperature, are stated for the eight fractions *A* to *H*. Densities were measured at 100°, and in each case the error is not greater than 2 in 10,000. The molecular weights were determined by the ebullioscopic method, using benzene as solvent ( $K = 2670$ ) in all but one instance, in which carbon disulphide had to be employed. The error of these determinations is within 1 per cent.

2. There is no doubt that fraction 12, No. *G*, Table II, which has a molecular weight corresponding with dotriacontane,  $C_{32}H_{66}$ ,

namely, 450, is an entirely different substance from the synthetic hydrocarbon. A redetermination of the molecular weight of fraction *G* gave 449 and 450.2, and a comparison of the refractive index of this fraction with that of synthetic dotriacontane showed a constant difference of 0.0014 over a range of 70–90°. In a later communication it will be shown that fraction *G*, on oxidation with air, gives a material containing 15 per cent. of oxygen, whereas the synthetic hydrocarbon was shown in the last paper to be unaffected by a similar treatment.

3. It will be seen that fraction 15, No. *H*, shows a value for the molecular weight which does not fall regularly in the series. This magnitude was redetermined, and in benzene found to be 434.3, and in carbon disulphide, 434.5. The synthetic hentriacontane,  $C_{31}H_{64}$ , obtained by Krafft, of molecular weight 434, showed a density at 98.4°/4° of 0.7619 compared with fraction *H* at 100°/4° of 0.7678, and a melting point of 68.1° compared with 66.6° for No. *H*.

Further, the solubilities and densities of the various fractions show a regularity, the lower the latter the greater the former, and to this the only exceptions are fraction 15, No. *H*, and synthetic dotriacontane.

In conclusion, it may be stated that we consider it not improbable that definite constituents have been isolated from paraffin wax, and that so far no evidence has been obtained for the existence in this material of normal hydrocarbons of the paraffin series.

The physical properties investigated, however, do not give sufficient data for the solution of the problem. The ultimate nature of the constituents can only be determined by chemical means, and such an investigation, by air oxidation at 100°, is now in progress.

Our thanks are due to the University Colston Society for grants towards the expenses of this work, and to the Department of Scientific and Industrial Research for assistance which enabled two of the authors (C. M. W. and R. W. W.) to take part in the investigation.

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CLXXXII.—*The Rôle of Protective Colloids in Catalysis. Part II.*

By THOMAS IREDALE.

LAST year the author (T., 1921, 119, 109) carried out some experiments on the inhibition of catalytic action by protective colloids, the particular reaction investigated being the catalytic decomposition of hydrogen peroxide by colloidal platinum. The most interesting colloid was gelatin, which exhibited a quite remarkable inhibitive action; but it seemed desirable to investigate the behaviour of gelatin solutions which had been prepared in two different ways, giving rise to particles of different size.

## EXPERIMENTAL.

The procedure adopted was very little different from that described in the previous paper. All the experiments were carried out at 25°, using well-cleaned, Jena-glass vessels and carefully purified water. Five c.c. of the reaction mixture were in each case titrated with about *N*/80-potassium permanganate, the rate of the unimolecular reaction being calculated directly from these titration figures. In the tables which follow, only the mean value, *k*, of the velocity "constant" for any particular reaction is given.\*

Two types of gelatin solution were prepared as follows, the material used being Coignet's photographic gelatin:

(a) A weighed amount of gelatin was allowed to swell for an hour in about one hundred times its weight of cold water, and after warming at 60° to effect complete dispersion, the solution was diluted with cold water to give a concentration of 0.04 per cent. Lower concentrations used in the experiments were obtained by simple dilution from this concentration. This type of solution will be called gelatin A.

(b) A 1 per cent. gelatin sol was prepared by allowing gelatin to swell for an hour in the requisite amount of water, and warming at about 60° to effect complete dispersion. The sol was then allowed to set to a gel † during the night, and on the next morning it was

\* It is necessary to emphasise at this stage that the average value of the velocity "constant" is useful for comparative purposes only if it is calculated from values obtained not much beyond the time for 50 per cent. decomposition.

† A 1 per cent. gelatin sol will not usually set unless there are traces of inorganic salts present, for example, those contained in gelatins of fairly high ash content. Although this foreign matter can have by itself no appreciable action on the platinum sols at such great dilution, its presence may markedly affect the size of particles of the gelatin sols, prepared in the two ways described.

shaken with a large volume of cold water to give a 0.04 per cent. solution; lower concentrations were obtained, as before, by simple dilution. This type will be called gelatin B. It is imperative that the solution be not excessively turbid, and it will be found better to prepare a sol of lower concentration than 1 per cent.—say, 0.6 per cent.—if the dispersion of the 1 per cent. gel is too difficult to effect in the cold. This will depend entirely on the nature of the gelatin used.

It is possible that the particles in gelatin B are somewhat larger than those in gelatin A. Zsigmondy ("Chemistry of Colloids," trans. by Spear, 1917, p. 224) maintains that such a difference can be detected with the ultramicroscope, anything approaching real homogeneity being found only with warm sols. That these two types behave somewhat differently in their effects on catalysis with colloidal platinum is evident from a large number of experiments carried out by the author. Table I records the results of some of these experiments, and the most striking facts appear to be the following:

(1) Since the results of series i. were obtained with the same platinum sol, having an activity denoted by the velocity constant 0.0263, it is evident that different gelatin solutions prepared in

TABLE I.

Cone. of gelatin per cent.	Series i.				Series ii.	
	k.		k.		k.	
	Gelatin A (i).	Gelatin B (i).	Gelatin A (ii).	Gelatin B (ii).	Gelatin A.	Gelatin B.
0	0.0263	0.0263	0.0263	0.0263	0.0365	0.0365
0.01	0.0062	0.0039	0.0044	0.0043	0.0057	0.0059
0.001	0.0065	0.0056	0.0056	0.0060	0.0070	0.0075
0.0001	0.0075	0.0077	0.0058	0.0098	0.0075	0.0088
0.00005	0.0102	0.0120	0.0096	0.0113	0.0090	0.0120
0.00001	0.0190	0.0178	0.0189	0.0229	0.0251	0.0276
0.000005	0.0213	0.0230	0.0216	0.0238	0.0288	0.0318

precisely similar ways do not always have the same inhibitive effect for each concentration investigated. This result might be anticipated, but, of the two types, gelatin A exhibits greater irregularities in behaviour. Dilution sometimes produces very little change in the activity of gelatin A solutions [this very pronounced effect is to be seen in Table II, with gelatin A (ii)], and it would appear that either the dilution results in an increase in the number of particles owing to subdivision or there is a tendency for an adsorption maximum to be reached in some particular cases.

(2) Gelatin B does not exhibit such a pronounced tendency to an adsorption maximum, and although subdivision of the particles may take place to some extent on dilution, it is not so noticeable.

TABLE II.

Conc. of gelatin per cent.	k.		
	Gelatin A (i).	Gelatin A (ii).	Gelatin B.
0	0.0185	0.0185	0.0185
0.01	0.0040	0.0050	0.0030
0.001	0.0053	0.0054	0.0045
0.0001	0.0061	0.0058	0.0066
0.00005	0.0068	0.0071	0.0086
0.00001	0.0123	0.0111	0.0146
0.000005	0.0151	0.0133	0.0180

At very low concentrations, gelatin B is always less effective than gelatin A as an inhibitor. This is quite in keeping with what is already known about gelatin, that its protective effect is greater the smaller the size of its particles. (Observation of the disappearance of inhibitive activity at different stages of dilution is the clue to the real relation between Zsigmondy's gold numbers and this interesting phenomenon, and will be discussed later.)

(3) Both types show a very rapid falling off in their activity below a concentration of about 0.00005 per cent. It may be that up to concentrations in this neighbourhood the adsorption process between the platinum and gelatin particles is largely electrocapillary in nature, but that above this concentration ordinary adsorption may be operating. If, for concentrations of gelatin above 0.00005 per cent., the logarithms of the gelatin concentrations be plotted against the logarithms of the percentage inhibition in each case, the curves obtained will be almost straight lines, and for gelatin A these lines will be more nearly horizontal than for gelatin B.

If gelatin A *does* consist of a large number of small particles, and gelatin B of a small number of larger particles, and if it is assumed that, on account of their higher surface energy, the smaller particles are more effective for adsorption, then one *would* expect an adsorption maximum to be reached more readily with gelatin A than with gelatin B, and the effects of gelatin B would fall off more rapidly with dilution.

It is too early in these investigations to state definitely just how these adsorption processes are operating in every case, but the results seem worth recording, as they are important for the study of the physico-chemical properties of gelatin.

Higher concentrations of gelatin than 0.01 per cent. have not been investigated, because viscosity changes in the solution would soon become appreciable, and the slowing down of the Brownian movement to any extent is a matter outside the present considerations.

Now, by varying both the gelatin and the platinum concentrations throughout any one experiment, some results have been

obtained which can be accounted for only on the adsorption theory. If diffusion plays such a large part in the catalysis as some people suppose, one would expect that a given concentration of gelatin would have a somewhat smaller effect on a fairly concentrated platinum sol than on a more dilute one, where the particles would be farther apart. But this is not by any means the case, and the ratios recorded in Table III show that the retardation in the velocity of reaction produced by a given quantity of gelatin is almost invariably greater the greater the concentration of the platinum sols, and this can be explained on no other ground than that of adsorption.

TABLE III.

Series i.			Series ii.			Series iii.		
Conc. of gelatin A per cent.	k.	Ratio.	Conc. of gelatin A per cent.	k.	Ratio.	Conc. of gelatin A per cent.	k.	Ratio.
Platinum sol A.			Platinum sol D.			Platinum sol H.		
0	0.0404	1	0	0.0834	1	0	0.1370	1
0.01	0.0070	0.17	0.001	0.0217	0.26	0.0001	0.0447	0.31
0.0001	0.0118	0.29						
0.00001	0.0270	0.67	Platinum sol E.			Platinum sol I.		
Platinum sol B			(conc. = $\frac{1}{2}$ Pt. sol D).			(conc. = $\frac{1}{16}$ Pt. sol H).		
(conc. = $\frac{1}{2}$ Pt. sol A).			0	0.0574	1	0	0.0055	1
0	0.0133	1	0.001	0.0152	0.26	0.0001	0.0020	0.39
0.01	0.0026	0.19	Platinum sol F					
0.0001	0.0054	0.40	(conc. = $\frac{1}{2}$ Pt. sol D).					
0.00001	0.0087	0.67	0	0.0312	1			
Platinum sol C			0.001	0.0102	0.32			
(conc. = $\frac{1}{2}$ Pt. sol A).			Platinum sol G					
0	0.0042	1	(conc. = $\frac{1}{2}$ Pt. sol D).					
0.01	0.0020	0.48	0	0.0114	1			
0.0001	0.0024	0.57	0.001	0.0027	0.24			
0.00001	0.0041	0.98						

Given a number of gelatin particles corresponding with a certain concentration, a greater proportion of these must be adsorbed by a large number of platinum particles than by a small number, but the exact quantitative relations existing can only be decided by more exact investigations. The difficulty is, to prepare gelatin solutions the ultramicros of which will not subdivide on dilution. One must be sure in every case that dilution of both the platinum and the gelatin merely affects the distribution and not the state of the particles.

With any other protective colloid, such as gum arabic, the same type of behaviour is exhibited, but gum arabic is not nearly so strong a protective colloid as gelatin, and its effects are not manifested at so great a dilution.



TABLE IV.

Conc. of gum arabic per cent.	Platinum sol J.		Platinum sol K.		Platinum sol L.	
	k.	Ratio.	k.	Ratio.	k.	Ratio.
0 .....	0.0243	1	0.0185	1	0.0052	1
0.1 .....	0.0131	0.54	0.0130	0.71	0.0043	0.82
0.01 .....	0.0167	0.69	0.0139	0.76	0.0047	0.90

(in concentration, sol J&gt;sol K&gt;sol L).

This brings up again the interesting point mentioned previously. Zsigmondy measured the quantity of protective colloid which was just insufficient to prevent coagulation of the gold sol by electrolytes. Expressed in milligrams per 10 c.c., this was called the gold number. Now it seemed desirable to find out what these limiting concentrations are in the case of the catalytic process. The gold numbers of several protective colloids were determined by Zsigmondy's method. The same solutions were then used in the catalytic experiments, and continually diluted until the effect of the colloid on the reaction was no longer perceptible. This was found not to be a very easy matter to decide, but from a large number of experiments on the same solutions, definite values for the limiting concentrations were finally obtained. They vary slightly, just as the gold number does, for different solutions of the same sample of protective colloid. Table V records one set of such measurements.

TABLE V.

Protective colloid.	Gold number.	Inhibition number per cent.	Gold number ratios.	Inhibition number ratios.
Gelatin .....	0.02	$2 \times 10^{-4}$	100	100
Egg-albumin .....	0.10	$1 \times 10^{-3}$	20	20
Dextrin .....	3	$2 \times 10^{-4}$	0.66	1
Starch .....	5	$6 \times 10^{-4}$	0.40	0.33

(In these determinations a platinum sol should be used which has a velocity constant between 0.02 and 0.01. The value 0.02 is the gold number for gelatin in the cold. Values as low as 0.004 and 0.005 can be obtained only at the temperature of the boiling solution.)

Giving to the most efficient protective colloid, gelatin, the value 100, and comparing the ratios of the gold numbers with the ratios of these limiting concentrations, the closest parallel is observed. It is proposed to call the limiting concentration in each case the "inhibition number," and this may be defined more strictly as—*that percentage of protective colloid which is just insufficient to inhibit catalytic action.*

Both the gold number and the inhibition number are evidently

a measure of the same property—the strength of the adsorbed film, and by this is meant the capacity of the protective colloid for inhibiting further adsorption.

A great many more protective colloids might have been investigated in this connexion and, indeed, the inhibition number will now be worked out for a large number of colloids using colloidal gold as catalytic agent, and it is anticipated that more exact relations will be found to hold; but it is easily seen that the above results are more than a coincidence, and illustrate very well the adsorptive theory previously upheld by Zsigmondy. He, however, did not attempt to explain completely the real significance of the gold number, and it is claimed that this work on catalysis has resulted in the first real attempt to do so. But the investigations have been confined to a single reaction, and they will have to be extended to numerous cases of colloid catalysis before the generalisations will seem really valid. At the same time, there is no reason to believe that this behaviour of protective colloids is peculiar only to the case of colloidal platinum and hydrogen peroxide; for the rate of reaction that is measured in these cases of heterogeneous catalysis seems really to be what might be called a velocity of adsorption, the chemical reaction at the surface of the catalyst probably being a very much faster process.

It is interesting in this connexion to note that Friend (T., 1921, 119, 932; this vol., p. 466) has recently been extending this work on protective colloids to other, more diverse, types of heterogeneous reactions, and the results he obtains are in agreement with the adsorptive theory.

The poisoning of colloidal metals protected by other colloids is a matter of great interest, but here the adsorption processes are much more complex, and the results that have been obtained so far are not very easy to interpret. But it seems that, fairly generally, a protected metal sol of the same activity as an unprotected one is not poisoned to the same extent by a given amount of catalytic poison, and this is what one would anticipate from the theory developed as the result of previous researches.

#### *Summary.*

Further experiments have been undertaken on the inhibition of catalysis by protective colloids, and the results of these experiments confirm the original idea, that adsorption is the controlling factor in the phenomenon.

An "inhibition number" has been obtained which is defined as "that percentage of protective colloid which is just insufficient to inhibit catalytic action," and the ratios of these numbers for

different protective colloids are of the same order of magnitude as the ratios of the gold numbers.

I am indebted to the Royal Commissioners of the Exhibition of 1851 for a scholarship which has enabled me to carry out this investigation, and to the Chemical Society for a grant which is defraying some of the attendant expenses.

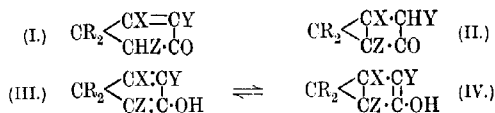
UNIVERSITY OF SYDNEY AND  
UNIVERSITY COLLEGE, LONDON.

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CLXXXIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part III. Intra-annular Tautomerism of  $\alpha$ -Campholytic Acid.*

By JUAN PEDIGE CHARLES CHANDRASENA, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

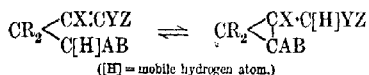
THE examples of intra-annular tautomerism previously discussed (T., 1920, 117, 1362; this vol., p. 128) are characterised most especially by the extraordinary facility with which the two individuals composing the tautomeric system must be assumed to undergo interconversion. In no case, indeed, has it yet been found possible to isolate more than one crystalline variety of any of these substances, which in solution exhibit reactions characteristic of both the structures (I) and (II) :



We may assume that the reason for this is the intimate connexion between the corresponding enolic forms (III and IV), which are valency-isomerides related to one another much like the two Kekulé individuals of a substituted benzene, and even more exactly like the bridged and double-bonded phases of the benzene nucleus by the aid of which the totality of aromatic transformations may, with large gain in uniformity, be interpreted (this vol., pp. 1133, 1143).

On general grounds, it may reasonably be said that the principal factor affecting the mobility of a tautomeric system is the simplicity of the mechanism of the isomeric change involved: valency-isomerides are more easily interconvertible than isomerides which

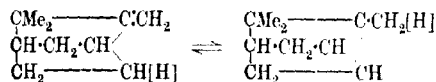
differ by the position of a hydrogen atom; the straight-chain, three-carbon system in the glutaconic esters is more mobile than the *cyclobutane* ring-chain three-carbon system (future communication), and so forth. If, therefore, means could be found of stopping the enolisation of the types (I) and (II), we should expect to observe a large decrease of mobility; for interchange between the bridged and double-bonded forms could now no longer occur by rearrangement of valencies alone, and the only available mechanism would be a *cyclopropane* ring-chain conversion



analogous to the *cyclobutane* changes referred to above. This change involves the migration of a hydrogen atom, and therefore we are led to anticipate that if the ketone groups in the types (I) and (II) were replaced by methylene groups the change



would occur only in the presence of acids or alkalis or at a high temperature. Such changes, occurring in the presence of reagents, are doubtless at the root of much that is difficult to understand in camphor chemistry; and, indeed, Meerwein and van Emster have already been forced to postulate an equilibrium between camphene and tricyclene in order to explain their observations on these compounds (*Ber.*, 1920, 53, [B], 1828):



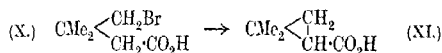
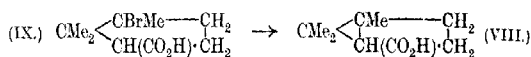
There are several well-known camphor derivatives belonging to type (V), one of the most familiar examples being  $\alpha$ -campholytic acid, the usual formula for which is (VII). Obviously, however, the bridged formula (VIII) has to be taken into account, for, in view of what is known with regard to such reactions, there seems to be no a priori reason why either or both of the converse changes



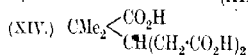
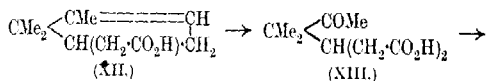
should not take place in the presence of suitable reagents.

The evidence usually quoted in favour of the accepted formula (VII) is far from satisfactory. The staple argument seems to be that Perkin and Thorpe obtained  $\alpha$ -campholytic acid by the action of alkalis on the bromocyclopentane acid (IX) (T., 1904, 85, 147).

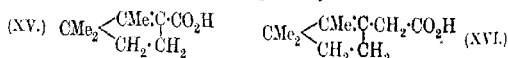
We know, however, that the production of a cyclopropane ring is the normal course of such a reaction.  $\gamma$ -Bromo- $\beta\beta$ -dimethylbutyric acid (X) gives dimethylcyclopropanecarboxylic acid (XI) (Blanc, *Bull. Soc. chim.*, 1905, [iii], **33**, 902),  $\alpha$ -bromo- $\beta\beta$ -dimethylglutaric acid gives caronic acid, and even  $\alpha$ -bromoglutaric acid, which might perhaps be expected to yield glutaconic acid, gives chiefly cyclopropanedicarboxylic acid on treatment with alkalis; so great is the tendency for the hydrogen atom adjacent to a carboxyl group to suffer elimination as hydrogen bromide in these cases. Perkin and Thorpe's synthesis of  $\alpha$ -campholytic acid from the  $\gamma$ -bromo-acid (IX) is therefore to be regarded as one of the strongest pieces of evidence against the formula which it is usually held to support; obviously, the elimination of hydrogen bromide from the acid (IX) should give rise to an acid of the bridged constitution (VIII), which, on other grounds, appears as a reasonable mode of formulation for  $\alpha$ -campholytic acid :



There remain, however, reasons for retaining formula (VII), the chief consisting in the analogy with  $\alpha$ -campholenic acid. No one, hitherto, appears to have succeeded in obtaining any definite oxidation products from  $\alpha$ -campholytic acid, but the constitution of  $\alpha$ -campholenic acid (XII) seems to be well established by its oxidation to ketoisocamphoric acid (XIII) and isocamphoric acid (XIV) (Tiemann, *Ber.*, 1896, **29**, 3014), the structure of which has been proved by synthesis (Perkin, T., 1899, **75**, 897) :



Both  $\alpha$ -campholytic acid and  $\alpha$ -campholenic acid undergo isomeric change on heating with mineral acids giving isolauronic acid (XV) and  $\beta$ -campholenic acid (XVI) respectively :

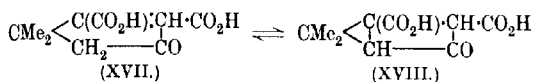


The constitutions of both these acids have been established by oxidation (Königs and Meyer, *Ber.*, 1894, **27**, 3466; Perkin, T., 1898, **73**, 802; Blanc, *Compt. rend.*, 1900, **130**, 840; Bouveault,

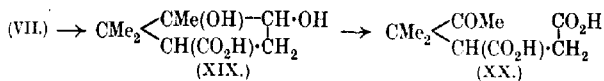
*Bull. Soc. chim.*, 1896, [iii], **19**, 565), and there can be no reasonable doubt as to the similarity of mechanism of the changes by which they are produced. These considerations strongly suggest the retention of formula (VII) for  $\alpha$ -campholytic acid owing to the analogy with the formula (XII) of  $\alpha$ -campholenic acid.

Considered collectively, then, the existing evidence relating to the structure of  $\alpha$ -campholytic acid is of a somewhat ambiguous character, and therefore it appeared desirable to apply to this acid the methods which were used in studying the cases of intra-annular tautomerism met with in the earlier investigations belonging to this series (*loc. cit.*). We have accordingly made a careful examination of the oxidation products obtained from  $\alpha$ -campholytic acid under a variety of experimental conditions.

It will be recalled that the acid (XVII), for instance, is oxidised by alkaline permanganate very smoothly in accordance with the double-bonded formula assigned to it, whilst evidence of the bridged form (XVIII) can be obtained by the use of cold ferricyanide, which oxidises it to caronic acid :



On oxidising  $\alpha$ -campholytic acid by alkaline permanganate, clear evidence was obtained of the unsaturated structure, the principal products being the dihydroxydihydro-acid (XIX) and  $\delta$ -keto- $\beta$ -carboxy- $\gamma\gamma$ -dimethylhexoic acid (XX) :



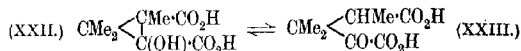
Similar results were obtained using alkaline chlorate in the presence of osmium tetroxide at 60°, but in this instance further evidence as to the mechanism of the oxidation was furnished by the isolation of  $\alpha\alpha$ -dimethyltricarballic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (XXI), which has been well characterised by other workers.

When, however,  $\alpha$ -campholytic acid was oxidised over a period of several weeks with cold acidified chlorate and osmium tetroxide, the product contained, not only all the above acids, but also two others the formation of which plainly points to the existence in acid solution of the bridged individual (VIII).

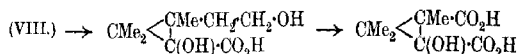
One of these was the acid  $\text{C}_8\text{H}_{12}\text{O}_6$ , usually called Balbiano's acid, the constitution of which has been very recently established by Kon, Stevenson, and Thorpe (this vol., p. 654), who have proved that this substance is a hydroxycyclopropane acid of the formula

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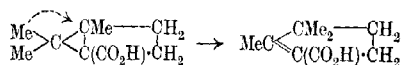
(XXII) in tautomeric relation with its open-chain isomeride (XXIII) and the lactonic modification of the latter :



It will at once be evident that neither of the individuals (XXII) or (XXIII) is capable of being represented as a direct oxidation product of the double-bonded form (VII) of  $\alpha$ -campholytic acid. On the other hand, the hydroxy-ring acid (XXII) is the normal oxidation product of the bridged individual (VIII) :

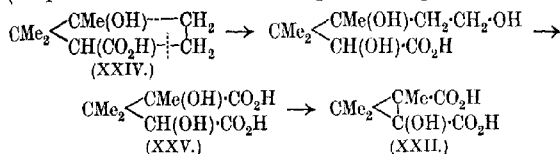


It appears significant, in view of the well-known influence of acids in accelerating the change from  $\alpha$ -campholytic acid into *isolauronic* acid, that Balbiano's acid was not produced, and, in fact, no evidence of the bridged individual of  $\alpha$ -campholytic acid was obtained, by oxidation in alkaline solution. The change from  $\alpha$ -campholytic acid into *isolauronic* acid is a most remarkable one if considered from the point of view of the double-bonded formula for  $\alpha$ -campholytic acid; it is, however, much more easily represented by the aid of the bridged formula (VIII), and in the earlier stages of these experiments we held the view that campholytic acid passes by way of its bridged form into *isolauronic* acid in the presence of acidic reagents :



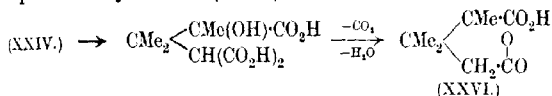
Towards the end of 1920, however, Meerwein and van Emster's paper appeared : these workers conclusively proved that tricyclene was not (as was then generally supposed) an intermediate product in the *isoborneol*-camphene transformation. About the same time, Professor Robinson told us of his explanation (since published, *Mem. Manchester Phil. Soc.*, 1920, 64, ii, 4) of the conversion of  $\alpha$ -campholytic acid into *isolauronic* acid. Now, although we do not find in the results of our own experiments any clear evidence for or against Robinson's explanation of the mechanism, there can be no doubt that, from the point of view chosen, it is the most detailed and strictly logical explanation that has yet been proposed, and therefore it is necessary to examine its bearing on the interpretation of the experiments here described. We need only consider Robinson's first stage, which consists in the addition of the elements of water to the double-bonded formula for campholytic acid. It will be evident that the hydroxy-acid (XXIV) formed in

this way is capable of undergoing oxidation (similarly to the bridged form of campholytic acid), giving a dihydroxy-acid (XXV) which would at once pass into the hydroxy-ring form of Balbiano's acid (compare Kon, Stevenson, and Thorpe, *loc. cit.*, p. 657):

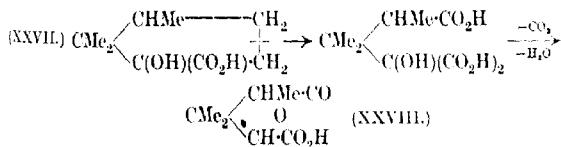


Evidently then, there are two alternative ways in which Balbiano's acid can be formed by oxidation, and therefore it became necessary to decide between them. This has been accomplished, and the results clearly show that, whatever may be the truth regarding the change which results in the formation of isolaunonic acid, the oxidation of  $\alpha$ -campholytic acid cannot be accounted for by any mechanism depending on the preliminary addition of water to the double-bonded individual as suggested by Robinson.

The hydroxy-acid (XXIV) is evidently capable of oxidation to a lactonic acid of the composition  $\text{C}_8\text{H}_{12}\text{O}_4$ , its structure being represented by formula (XXVI):



This lactonic acid is therefore to be regarded as capable of being derived from the double-bonded form of campholytic acid by addition of water and then oxidation. On the other hand, the bridged individual could, by a corresponding series of transformations, yield two such lactonic acids, corresponding with the two ways in which hydrolytic fission can occur at the bridge. According to one mode of fission, the primary product would be the hydroxy-acid (XXIV), and the ultimate oxidation product the lactonic acid (XXVI). According to the other mode, the primary product would be the isomeric hydroxy-acid (XXVII), and the ultimate product the lactonic acid (XXVIII):



The lactonic acid (XXVI) may be formed, therefore, from either



modification of campholytic acid, but the lactonic acid (XXVIII) can only be obtained from the bridged individual. The lactonic acids (XXVI and XXVIII) are known and have very similar properties. However, the lactonic acid obtained along with Balbiano's acid by the oxidation of  $\alpha$ -campholytic acid by cold chlorate and osmium tetroxide in acid solution was conclusively proved to have the structure (XXVIII) by direct comparison with a synthetic specimen. The production of this lactonic acid along with Balbiano's acid appears to leave no room for doubt as to the existence in acid solution of the bridged individual of campholytic acid.

#### EXPERIMENTAL.

The  $\alpha$ -campholytic acid required for these experiments was prepared from sodium ethyl camphorate by the electrolytic method described by Walker (T., 1893, **63**, 475; 1895, **67**, 347; 1900, **77**, 383). This process was found to be much more convenient than the method of Noyes (*Amer. Chem. J.*, 1894, **16**, 310; 1895, **17**, 424; 1900, **24**, 290), depending on the action of bromine and alkali on camphoramic acid.

(A.) *Oxidation of  $\alpha$ -Campholytic Acid by Cold Alkaline Permanganate; Formation of  $\gamma\delta$ -Dihydroxydihydrocampholytic Acid and  $\delta$ -Keto- $\beta$ -carboxy- $\gamma\gamma$ -dimethylhexoic Acid.*

The  $\alpha$ -campholytic acid (7 grams), dissolved in 25 c.c. of 2*N*. aqueous sodium carbonate, was treated with 3.16 per cent. aqueous potassium permanganate until no further decoloration took place in the cold. The quantity of permanganate decolorised corresponded with the absorption of three atoms of oxygen. The suspension was boiled and filtered, and the oxides of manganese thoroughly exhausted by suspending in water and passing a current of steam. The combined aqueous filtrates were acidified with hydrochloric acid, evaporated to a small bulk, and extracted with ether. The mixture of acids obtained in this way slowly set to a paste of crystals, which were drained as thoroughly as possible on porous porcelain, and then triturated with ether.

*$\gamma\delta$ -Dihydroxydihydro- $\alpha$ -campholytic Acid.*—The constituent insoluble in cold dry ether was crystallised, first from a large quantity of boiling ether, and then from ethyl acetate, and separated in large, lustrous prisms, m. p. 159–160°. It was identified by analysis and by direct comparison with the dihydroxy-acid obtained by the oxidation of  $\alpha$ -campholytic acid with sodium chlorate and osmium tetroxide (Found: C = 57.6; H = 8.5.  $C_9H_{16}O_4$  requires C = 57.4; H = 8.5 per cent.).

The *diacetyl* derivative was prepared by boiling the acid with an

excess of acetyl chloride for half an hour, after which the evolution of hydrogen chloride had ceased. The solution was evaporated over solid potassium hydroxide in an evacuated desiccator, and the crystalline residue purified by crystallisation from a mixture of light petroleum and ether. It separated in small needles, m. p.  $122^{\circ}$ , which were very soluble in all the usual solvents excepting water and light petroleum (Found: C = 57.7; H = 7.6.  $C_{13}H_{20}O_6$  requires C = 57.3; H = 7.3 per cent.).

*$\delta$ -Keto- $\beta$ -carboxy- $\gamma\gamma$ -dimethylhexoic Acid.*—The acid which dissolved in the cold dry ether (above) slowly solidified when the solvent had evaporated. It was crystallised first from ether and then from ethyl acetate, and was obtained in needles, m. p.  $119$ – $121^{\circ}$ . It was identified with the substance (p. 1551) obtained by oxidation with sodium chlorate and osmic acid (Found: C = 54.2; H = 7.3.  $C_9H_{14}O_5$  requires C = 53.5; H = 6.9 per cent.). Sufficient material was not available for an extended examination, but the substance certainly appeared to yield condensation products with the usual reagents for ketones.

(B.) *Oxidation of  $\alpha$ -Campholytic Acid by Means of Sodium Chlorate and Osmium Tetroxide in Alkaline Solution at  $60^{\circ}$ ; Formation of  $\gamma\delta$ -Dihydroxydihydrocampholytic Acid and  $\alpha\alpha$ -Dimethyltricarballic Acid.*

A solution of  $\alpha$ -campholytic acid (5 grams) in a small excess of 2N-aqueous sodium hydroxide was mixed with an aqueous solution (250 c.c.) of sodium chlorate (20 grams) and osmium tetroxide (0.3 gram). The mixture was kept in a thermostat at  $60^{\circ}$  for thirty-six hours, then acidified by means of hydrochloric acid, evaporated to a small bulk, and extracted with ether. The residue which was left when the ether had evaporated rapidly solidified. On triturating with cold dry ether, an insoluble residue remained, which, after several crystallisations from ethyl acetate, yielded the dihydroxy-acid (p. 1548) in a state of purity. The other main constituent of the product insoluble in ether was an acid, m. p.  $170^{\circ}$ , which contained chlorine and was not further investigated.

*$\alpha\alpha$ -Dimethyltricarballic Acid.*—The portion of the oxidation product soluble in cold dry ether was recovered as a gum, which refused to solidify. It was therefore dissolved in barium hydroxide solution, and the sparingly soluble barium salts were collected and decomposed by means of hydrochloric acid. The regenerated acids, which were isolated by extraction with ether, were obtained in a crystalline condition by rubbing with cold chloroform, and then crystallised twice from water. The product obtained in this way formed minute prisms, m. p.  $156$ – $157^{\circ}$ , and was identified

as dimethyltricarballic acid by analysis (Found: C = 47.0; H = 6.1. Calc., C = 47.1; H = 5.9 per cent.), and by a careful comparison of its properties with the descriptions given by Barthe (*Compt. rend.*, 1897, **125**, 183) and by Haller and Blanc (*ibid.*, 1900, **131**, 21).

(C.) *Oxidation of  $\alpha$ -Campholytic Acid by Means of Chloric Acid and Osmic Acid in Acid Solution at 20°; Formation of  $\gamma$ , $\delta$ -Dihydroxy-dihydrocampholenic Acid,  $\delta$ -Keto- $\beta$ -carboxy- $\gamma$ -dimethylhexoic Acid, the Lactone of  $\gamma$ -Hydroxy- $\alpha\beta\beta$ -trimethylglutaric Acid,  $\gamma$ -Keto- $\alpha\beta\beta$ -trimethylglutaric Acid, and  $\alpha$ -Dimethyltricarballic Acid.*

$\alpha$ -Campholytic acid (30 grams) was mixed with a solution of sodium chlorate (95 grams), glacial acetic acid (20 grams), and osmium tetroxide (1 gram) in 1500 c.c. of water. The mixture was kept at the ordinary temperature for several weeks, then filtered from a small amorphous deposit, and evaporated to dryness. The residue was evaporated twice with water in order to remove acetic acid, and then dissolved in water and extracted with ether. The residue from the ether was left until it had solidified, and was then boiled with dry ether in order to separate the main bulk of the sparingly soluble dihydroxy-acid. The residue from the ether was seeded with a trace of the original mixture and allowed to resolidify (this took several days), and then triturated with cold benzene until the more soluble portion appeared to have been completely removed.

*Lactone of  $\gamma$ -Hydroxy- $\alpha\beta\beta$ -trimethylglutaric Acid.*—The acids which were sparingly soluble in benzene were subjected to repeated fractional crystallisation from benzene and ethyl acetate employed alternately. In this way three products were obtained: (i) the dihydroxy-acid mentioned above, m. p. 159–160°; (ii) an acid which separated from benzene in long needles, m. p. 165–166°; (iii) an acid product, m. p. 148–150°. The last crystallised as a single substance and was free from chlorine, but its carbon and hydrogen content did not correspond with any definite formula, so that it was ultimately supposed to be a mixture and its investigation was abandoned. The substance, m. p. 165–166°, gave figures corresponding with the formula  $C_8H_{12}O_4$ , and on titration (by dissolving in excess of alkali and titrating the excess) behaved as a dibasic acid. It was at first supposed that this substance was  $\alpha$ -methylcaronic acid (trimethylcyclopropanedicarboxylic acid), but on further investigation it was discovered that, when titrated by the direct method, the substance behaved as a monobasic acid, and, in fact, had all the properties of a lactone. Ultimately it was

identified with the lactonic acid which Balbiano prepared first by reduction of his oxidation product  $C_9H_{12}O_5$  of camphoric acid (*Ber.*, 1894, 27, 2136) and later by elimination of hydrogen bromide from  $\gamma$ -bromo- $\alpha\beta$ -trimethylglutaric acid (*Atti R. Accad. Lincei*, 1899, [v], 8, I, 426), by direct comparison and the mixed-melting-point test with a specimen obtained by the second of Balbiano's methods [Found: C = 55.8; H = 7.0. Calc., C = 55.8; H = 7.0 per cent. Equivalent (direct titration) = 171. Calc. 172. Equivalent (back titration) = 86.7. Calc. 86].

*$\gamma$ -Keto- $\alpha\beta\beta$ -trimethylglutaric Acid.*—The acids which dissolved in cold benzene showed but little tendency to crystallise, and therefore were dissolved in a small excess of barium hydroxide and the insoluble barium salts collected. The main constituent of the acids regenerated from these insoluble salts was  $\alpha\alpha$ -dimethyltricarballic acid (above). The soluble barium salts were decomposed with hydrochloric acid and the organic acids extracted with ether, and, after evaporating the ether, mixed with chloroform, which caused the separation in the crystalline state of a small amount of the ketonic acid described on p. 1549. The gummy acids were dissolved in an exact equivalent of ammonia, treated with calcium chloride, and the solution evaporated to a small bulk. The salt which separated was collected after cooling, washed with cold water, and decomposed with hydrochloric acid. The regenerated acid solidified fairly readily, but as it did not appear to crystallise well from solvents, was prepared for analysis by washing with chloroform. It was identified by its melting point, 119–120°, by analysis (Found: C = 51.3; H = 6.6. Calc., C = 51.1; H = 6.4 per cent.), by its conversion on heating with sulphuric acid into trimethylsuccinic anhydride, by the melting point of its condensation product with *o*-phenylenediamine, and, finally, by direct comparison and a mixed-melting-point determination with the substance described by Kon, Stevenson, and Thorpe (this vol., p. 663).

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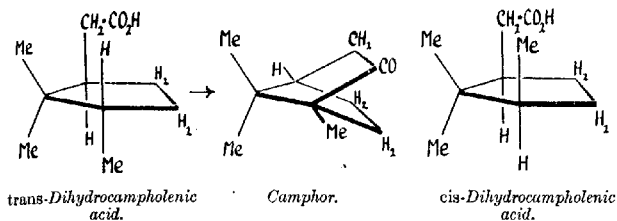
CLXXXIV.—*Effect of Attached Groups on the Ease of Formation of the cyclopentane Ring.*

By JUAN PEDIGE CHARLES CHANDRASENA and CHRISTOPHER KELK INGOLD.

THE broad fact that ease of ring formation reaches a maximum in *cyclopentane* and *cyclohexane* compounds is in good general agreement both with the original strain hypothesis of Baeyer and the modification of it which was recently suggested (Ingold, T., 1921, 119, 305) as being more closely in accordance with experimental data and more reasonable on general grounds. The size of the homocyclic ring, however, is by no means the only factor which influences ease of formation, and it is only by means of the modified strain hypothesis that it becomes possible to trace the influence of attached carbon chains on the ease of formation of a given type of ring. Reference has already been made (*loc. cit.*) to the striking effect of the *gem*-dimethyl group, and of quaternary groupings in general, in assisting the closure and augmenting the stability of those rings (*cyclopropane*, *cyclobutane*, and *cyclopentane* rings) the internal angles of which are less than  $115.3^\circ$ ; reference has been made also to the manner in which such groupings are disposed in natural products so as to relieve to a maximal extent the strains inherent in the ring-system (T., 1921, 119, 951). The matter is very well illustrated as regards *cyclopentane* ring-formation by the conversion of substituted acids of the adipic acid series into *cyclopentanones*. Using a standard method of ring closure, Blanc found (*Compt. rend.*, 1907, 144, 1356) that  $\alpha\alpha$ -dimethyladipic acid was converted into dimethyl*cyclopentanone* much more smoothly than adipic acid is into *cyclopentanone*, and Perkin and Thorpe showed (T., 1904, 85, 138) that  $\gamma$ -carboxy- $\alpha\alpha$ -dimethyladipic acid gave the corresponding *cyclopentanone*-acid in quantitative yield when its sodium salt was boiled with acetic anhydride, a method of ring closure which fails when applied to adipic acid.

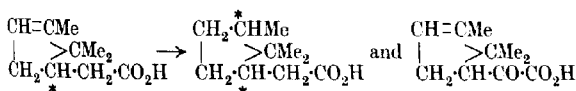
In these cases only one *gem*- or quaternary grouping was present in the open-chain acid and in the *cyclopentanone* formed. It is to be expected on the basis of the hypothesis outlined (*loc. cit.*) that the introduction of a second quaternary grouping would materially enhance the tendency towards ring-closure, and in the present paper a case is described in which the formation of a *cyclopentanone* takes place with quite extraordinary facility under the influence of two quaternary groupings. The substituted *cyclopentanone* was compared, the general stability and ease of formation of which appear

to be guaranteed by its wide occurrence in nature (*loc. cit.*). The open-chain acid was *trans*-dihydrocampholenic acid, which, when obtained by reduction of campholenic acid, passes spontaneously into camphor in aqueous solution at 60° :



Mahla and Tiemann (*Ber.*, 1900, **33**, 1934) obtained a dihydrocampholenic acid by hydrolysis of the nitrile prepared from camphorimine. No configuration was assigned to this acid, but, in view of its stability, there can be no doubt that it is the *cis*-modification. It will be evident from the space formulæ (above) that the *cis*-acid is not capable of undergoing conversion into camphor in the same way as the *trans*-acid.

The method employed in order to reduce the campholenic acid was an unusual one; the acid was warmed at 60° with an aqueous solution of calcium hydroxide containing silver oxide in suspension. There are a number of examples on record which prove that silver oxide frequently gives products of reduction of compounds that are difficult to reduce in any other way (compare T., 1915, **115**, 1098). In the present instance, however, the dihydro-acid, or rather the camphor into which it passed by loss of water, was not the sole or even the chief product of the reaction, since a large proportion of the material became oxidised to a ketonic acid. This acid, which has the composition C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>, is unsaturated, gives a semicarbazone, and behaves towards concentrated sulphuric acid like an  $\alpha$ -ketonic acid; there appears to be no doubt that it is  $\alpha$ -ketocampholenic acid.



It will be noted that campholenic acid contains but one asymmetric carbon atom (\*), on which alone its optical activity must depend. Dihydrocampholenic acid contains two asymmetric carbon atoms (each marked \*), and it might therefore be expected that, unless something having the nature of an "asymmetric synthesis"

has occurred, the acid would be externally compensated as regards the carbon atom rendered asymmetric by reduction. Camphor contains two asymmetric carbon atoms corresponding with the two in the dihydro-acid. Now the synthetic camphor was optically active, and, in fact, indistinguishable from ordinary natural camphor, the activity of which depends on both the asymmetric carbon atoms which it contains. An examination of the space formulæ shows that this result is really in agreement with stereochemical theory despite the fact that it involves the production of a second asymmetric carbon atom without any external compensation. It is ring-formation, of course, that is responsible for the apparent anomaly, and it should be possible to base a method of resolution of externally compensated compounds on the principle which is involved.

#### EXPERIMENTAL.

Optically active  $\alpha$ -campholenic acid was prepared from *d*-camphoroxime through the nitrile as described by Tiemann (*Ber.*, 1895, 28, 2166).

A mixture of  $\alpha$ -campholenic acid (2 grams), silver oxide (5 grams), calcium oxide (1 gram), and water (50 grams) was heated for seven days at 60° in a thermostat, the flask being fitted with a specially designed condenser-trap in order to prevent any crystalline sublimate from returning to the solution. The solution was decanted from the thick deposit of silver, faintly acidified with sulphuric acid, concentrated to a small bulk, and extracted with ether.

*d*-Camphor.—The whole of the camphor generated during the reaction collected in the trap, no trace remaining in the aqueous liquid. The dried ketone melted at 175° without recrystallisation or resublimation and therefore was practically pure. It was shown to be identical with natural *d*-camphor by direct comparison: both had the same m. p. (175°), which was not depressed on mixing the two specimens; both had the same specific rotation ( $[\alpha]_D = 44^\circ$  in alcohol); each gave an oxime (prepared by Nageli's method, *Ber.*, 1883, 16, 497) which had m. p. 120°, the m. p. of a mixture of both being 120° also.

$\alpha$ -Keto- $\alpha$ -campholenic Acid.—The residue from the ether extract was obtained in a crystalline condition and then recrystallised from dry ether. The ketonic acid separated in small cubes, m. p. 125–126° (Found: C = 65.2; H = 7.7.  $C_{10}H_{14}O_3$  requires C = 65.9; H = 7.7 per cent.). The acid instantly decolorises cold alkaline permanganate, and gives the usual reactions for ketones. On warming with concentrated sulphuric acid, it evolves carbon monoxide in the manner characteristic of  $\alpha$ -ketonic acids (0.0082

gram gave 32.8 c.c. of CO at 27.5° and 760 mm., that is 29.8 c.c. at *N.T.P.*  $C_8H_{13}CO \cdot CO_2H$  requires CO = 28.1 c.c. at *N.T.P.*). The product which remained in solution in the sulphuric acid was neither  $\alpha$ -campholytic acid nor  $\beta$ -campholytic acid, but consisted chiefly of an uncrystallisable gum. Probably  $\alpha$ -campholytic acid, the normal product of this decomposition, was formed intermediately, as a specimen of this acid, prepared by electrolysis of sodium ethyl camphorate (Walker, T., 1893, 63, 495), was found to give a very similar gum when heated with concentrated sulphuric acid under the same conditions.

The *semicarbazone* was prepared by treating an aqueous-alcoholic solution of the acid with concentrated aqueous semicarbazide acetate. It crystallised from alcohol in colourless needles, m. p. 214° (Found: N = 17.7.  $C_{11}H_{17}O_3N_3$  requires N = 17.6 per cent.).

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## CLXXXV.—*The Calculation of the Colour of the Azo-dyes and Related Coloured Substances.*

By JAMES MOIR.

THE method of representing coloured substances by hydroxylated formulae which may then be "dissected" into a fundamental skeleton (or parent-substance) and a number of subsidiary groups or linkages (Moir, T., 1921, 119, 1655) has now been applied with success to the simpler azo-dyes, and numerical values have been found for the required linking-factors, whereby, for example, the colour of ionised benzeneazophenol,  $Ph \cdot N \cdot N \cdot \text{C}_6H_4 \cdot O'$ , may be calculated from that of ionised phenol as parent substance.

### *Hydroxy-compounds.*

Pursuing this example, benzeneazophenol is written as either  $Ph \cdot N(OH) \cdot NH \cdot C_6H_4 \cdot O'$  or  $Ph \cdot NH \cdot N(OH) \cdot C_6H_4 \cdot O'$ , and the method of calculation is the same as before: the figure representing the wave-length of the absorption band of ionised phenol ("phenoxide ion,"  $\lambda$  287) is multiplied successively by (1) the "imino-interposition-factor" 1.090, (2) the "oximino-interposition-factor" 1.200, and (3) the monocyclic phenyl factor previously found (*loc. cit.*, p. 1660) 1.135. The result,  $\lambda_x = 287 \times 1.09 \times 1.20 \times 1.135 = 426$ , is the wave-length of the absorption band of the benzeneazophenol ion. Observation (in water) shows that the centre



of the band (which is quite broad as compared with those of dieyclic substances) lies at about  $\lambda$  427.

In the previous paper, it was shown that the process of calculating the colour of a complicated substance involves incidentally the calculation of the colour of all the substances lying between the original and the parent substance (*loc. cit.*, p. 1658).

Applying this principle here, we calculate:—

$$(1) \text{NH}_2\text{N}(\text{OH})\text{C}_6\text{H}_4\text{OH} \text{ or } \text{NH}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}; \quad \lambda_z = 287 \times 1.09 \times 1.20 = \lambda 376.$$

$$(2) \text{Ph}\cdot\text{N}(\text{OH})\text{C}_6\text{H}_4\text{OH} \text{ or } \text{PhN}\cdot\text{C}_6\text{H}_4\text{:O} \text{ (quinoneanil)}, \quad \lambda_z = 287 \times 1.20 \times 1.135 = \lambda 392.$$

$$(3) \text{H}\cdot\text{N}(\text{OH})\text{C}_6\text{H}_4\text{OH} \text{ or } \text{NH}\cdot\text{C}_6\text{H}_4\text{:O} \text{ (quinoneimide)}, \quad \lambda_z = 287 \times 1.20 = \lambda 345.$$

The first of these substances does not appear to have been made; observations on the other two agree sufficiently well with the calculation. In addition, calculation can be made of (4) *p*-aminophenol:  $\lambda_z = 287 \times 1.09 = \lambda 313$ ; (5) *p*-hydroxydiphenylamine:  $\lambda_z = 287 \times 1.09 \times 1.135 = \lambda 356$ ; and (6) *p*-hydroxyphenylhydrazine:  $\lambda_z = 287 \times (1.09)^2 = \lambda 341$ , but since these are leuco-compounds, it is uncertain at present whether they can be made to exhibit the required absorption by choosing a suitable solvent and hydron-concentration.

#### Amino-compounds.

By applying the monocyclic colour factors already discovered (*loc. cit.*, p. 1660), the aminoazo-dyes and their *N*-methyl derivatives can also be calculated as regards colour.

On the page referred to, the amino-factor is given as 1.14 and the dimethylamino-factor as 1.222. I now find from a closer scrutiny of all the compounds that there are really two partly-superposed absorption bands in all these substances, which sometimes coalesce almost completely, giving the impression of one broad band (50  $\mu$  wide), for which the above factors 1.14 and 1.222 were calculated.

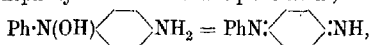
The real amino-factor is 1.10 and 1.18 and the real dimethylamino-factor is 1.19 and 1.27, the lower number referring to the lower band and the higher number to the higher band in each case.

Applying these to the foregoing hydroxy-compounds, we calculate:

$$(a) \text{ } p\text{-Aminoazobenzene}, \quad \lambda_z = 287 \times 1.09 \times 1.20 \times 1.135 \times (1.10 \text{ and } 1.18) = \lambda \lambda 469 \text{ and } 503. \text{ Observation gives, in slightly}$$

acid solution, a broad band with centre at about 497, really two vague bands at 478 and 510 overlapping. This agreement is not so good as in the case of the others.

(b) Quinonephenyldi-imine or iminoquinoneanil,



is the foregoing minus the NH linkage,  $\lambda_x = (469 \text{ and } 503)/1.09 = \lambda\lambda 430 \text{ and } 462$ . This substance was observed to have  $\lambda 450$  broad when acidic, but there are probably two bands at 430 and 465 overlapping.

(c) *p*-Aminophenylhydroxylamine,  $\text{NH}(\text{OH})\langle\bigcirc\rangle\text{NH}_2 = \text{hydrated quinone-di-imine}$ ,  $\lambda_x = 287 \times 1.20 \times (1.10 \text{ and } 1.18) = \lambda\lambda 380 \text{ and } 408$ .

This also agrees sufficiently well with observation, but the substance is too unstable in acidified water to be examined, as it changes to azoaniline. The free substance, Willstätter's quinonedi-imine, was observed photographically to have  $\lambda$  about 340 in ethereal solution.

The calculated values for (d) *p*-phenylenediamine and (e) *p*-aminodiphenylamine are respectively  $\lambda\lambda 344$  and 370 and  $\lambda\lambda 392$  and 420, but the colours appear to be latent in these leuco-compounds.

#### Dimethylamino-compounds.

The following are calculated, using the factors given on p. 1556.

(f) Dimethylaminoazobenzene (butter-yellow):  $\lambda_x = 426^* \times (1.19 \text{ and } 1.27) = \lambda\lambda 507 \text{ and } 541$ . Observation gives  $\lambda\lambda 508$  and 543, the two bands being well separated. Closer agreement between theory and observation is not to be expected until the third place of decimals in the colour-factors shall have been ascertained.

(g)  $\text{Ph}\cdot\text{N}(\text{OH})\langle\bigcirc\rangle\text{NMe}_2 = \text{Ph}\text{N}:\langle\bigcirc\rangle:\text{NMe}_2\text{Cl}$ . The calculated bands are  $\lambda\lambda 466$  and 497.

(h)  $\text{NH}(\text{OH})\langle\bigcirc\rangle\text{NMe}_2$ . The calculated bands are  $\lambda\lambda 411$  and 438.

By observation, the main band of this substance is at  $\lambda 670$ , but there is also a faint band at about  $\lambda 430$ .

Next, by introducing monocyclic substitution-factors analogous to those given in A., 1921, 120. ii. 6, we may calculate the colour of methyl-orange, methyl-red, etc. The *p*-sulphonic acid-factor is 0.98, the *m*-sulphonic acid-factor is 0.99, and the *o*-sulphonic acid-factor is about 1.02. The corresponding *p*-, *m*-, and *o*-carb-

\*  $\lambda$  for benzenesazophenol already ascertained.

oxyl factors are closer to unity, namely, about 0.99, 0.995, and 1.01, respectively. The factors are larger when the groups are in the other ring, that is, in that containing the auxochrome group, for example, 1.05 for carboxyl meta to the auxochrome and ortho to the linkage (*loc. cit.*, p. 1660, B of first table).

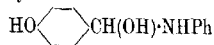
Methyl-orange: Calculated  $\lambda$  497 and 530. Observed  $\lambda$  498 and 534.

Methyl-red: Calculated  $\lambda$  512 and 547. Observed  $\lambda$  514 and 548.

*Coloured Substances Related to the Azo-dyes.*

At the beginning of this paper two "interposition-factors" were given by means of which the colours of all the foregoing substances have been calculated. By introducing now two more factors of this kind, namely, the "methylene-interposition-factor" (value 0.92) and the "carbinol-interposition-factor"  $-\text{CH}\cdot\text{OH}-$  (value 1.01), we can calculate the azomethine and the stilbene colours.

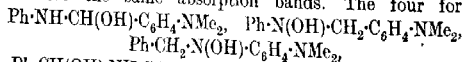
(1) *p*-Hydroxybenzylideneaniline is written



or  $\text{HO} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2\cdot\text{N}(\text{OH})\text{Ph}$ . From the first formulation, the calculated band is  $287 \text{ (phenoxide)} \times 1.01 \text{ (carbinol)} \times 1.09 \text{ (imino)} \times 1.135 \text{ (phenyl)} = \lambda 358$ ; from the second formulation, the calculation is  $287 \times 0.92 \times 1.20 \times 1.135 = \lambda 358$  also. In fact, the ratio of the oxidised to the unoxidised linkages, namely,  $\text{CH}\cdot\text{OH}/\text{CH}_2$  and  $\text{NOH}/\text{NH}$ , is the same, namely, exactly 11/10. It follows from this that the isomeric substance benzylidene-*p*-aminophenol,  $\text{Ph}\cdot\text{CH}\cdot\text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH}$ , which, when written in the

hydroxylated form, becomes either  $\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{NH} \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH}$  or  $\text{Ph}\cdot\text{CH}_2\cdot\text{N}(\text{OH}) \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH}$ , must have the same absorption band as *p*-hydroxybenzylideneaniline. Observation shows this to be the case, both substances possessing a band at about  $\lambda 360$ .

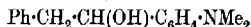
(2) *p*-Dimethylaminobenzylideneaniline and benzylidene-*p*-aminodimethylaniline constitute another pair of different azomethines which have the same absorption bands. The four formulae



and  $\text{Ph}\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , may be employed to calculate the bands, all giving the same result, namely,  $\lambda_x = 358$  (the hydroxy-compound above)  $\times (1.19 \text{ and } 1.27) = \lambda\lambda 427 \text{ and } 456$ . Observa-

tion shows that both substances have bands at about  $\lambda\lambda$  430 and 457.\*

(3) *p*-Dimethylaminostilbene. This is written as



and gives calculated values for the bands  $\lambda\lambda$  360 and 385. Observation shows that only the lower band is present ( $\lambda$  360). The two-banded spectrum of the aminoazo-dyes has disappeared when only one nitrogen atom is present in the molecule; it is therefore probably due to two simultaneous orbits, one passing from the auxochrome to the nearer nitrogen atom and the other from the auxochrome to the outer nitrogen atom.

(4) *p*-Hydroxystilbene. This gives the calculated value  $\lambda$  302. Hewitt, Lewcock, and Pope (T., 1912, **101**, 609, curve IV) give  $\lambda$  329 as the value for the substance in alkaline solution, and  $\lambda$  308 for the substance in neutral alcoholic solution. This must be classed as a disagreement with theory, because it is the alkaline phase which should agree with the calculation.

We can next calculate the colour of all the important substances lying between the azomethines (or stilbenes) and the parent substance.

Name and Formula.	$\lambda$ Calc.	$\lambda$ Obs.
(a) <i>p</i> -Hydroxybenzaldimine, HO-C <sub>6</sub> H <sub>4</sub> ·CH·NH <sub>2</sub> or methylene- <i>p</i> -aminophenol, HO-C <sub>6</sub> H <sub>4</sub> ·N·CH <sub>2</sub>	316 for both	—
(b) <i>p</i> -Hydroxybenzhydrol, Ph·CH(OH)·C <sub>6</sub> H <sub>4</sub> ·OH	329*	—
(c) Quinomethane, HO< >CH <sub>2</sub> ·OH or CH <sub>2</sub> < >O	291*	—
(d) Quinol, OH< >OH (divide foregoing by CH <sub>2</sub> -factor)	316	296 un-ionised
(e) <i>p</i> -Dimethylaminobenzhydrol, Ph·CH(OH)·C <sub>6</sub> H <sub>4</sub> ·NMe <sub>2</sub>	392 and 418	400 broad
(f) <i>p</i> -Dimethylaminobenzophenone, Ph·CO·C <sub>6</sub> H <sub>4</sub> ·NMe <sub>2</sub>	about 329	—
(g) <i>p</i> -Dimethylaminostyrene, CH <sub>2</sub> ·CH·C <sub>6</sub> H <sub>4</sub> ·NMe <sub>2</sub>	317	—
(h) <i>p</i> -Hydroxybenzaldehyde, HO< >CH(OH)·OH	320	330 (alc.) †
(i) <i>p</i> -Nitrosophenol, HO< >N(OH)·OH	379	415 (alc.) †
(j) <i>p</i> -Dimethylaminobenzaldehyde	381	371 and 355 { aqueous acetic acid
(k) <i>p</i> -Nitrosodimethylaniline	452	457
(l) <i>p</i> -Dimethylaminobenzoic acid acetate		about 330
(m) <i>p</i> -Nitrophenol salt		405 (alc.) †

\* This is the same result as before (Moir, *loc. cit.*, p. 1660, bottom).

† Observations by Baly and Tuck.

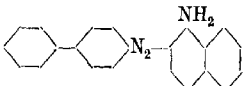
\* Benzylidene-*p*-aminodimethylaniline, however, exhibits a higher colour (with two bands at  $\lambda\lambda$  517 and 480) when dissolved in glacial acetic acid, in this respect differing from its isomeride.

We see, therefore, that the whole family has thus been connected with the previous work on fuchsone and the monocyclic phthaleins. In that work the parent substance was quinomethane (*c* in the above table), which is quinol with the "methylene-interposition-factor." Using the other three interposition-factors, we get three other prototype substances, namely, *p*-hydroxybenzaldehyde, quinoneimide, and *p*-nitrosophenol, and from these in turn, by use of the other interposition-factors, we reach the stilbene, azo-methine, and azo-families.

#### *The Higher Azo-dyes.*



These do not differ much from the lower ones; the main effect of complexity is a broadening of the bands with only a slight shift towards the red. Thus benzeneazobenzeneazophenol (in alkali) is lower in colour than (but very similar to) dimethylaminoazo-benzene. The extra  $C_6H_5N_2$  group is to be regarded as a mere load or substituent on the phenyl ring of the simple azo-dye, and all load-factors are known to be not much greater than unity. Similarly with the naphthalene compounds, the effect is comparatively small and is due to loading. The factor for both  $C_6H_5N_2$  and for naphthalene/benzene is about 1.15.

Similarly, congo-red and the other benzidine dyes have colours

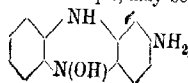
corresponding with , etc., in the simple

series. The colours of the dicyclic azo-dyes can be calculated from the dicyclic factors, remembering that the oxidation factor is 0.6 (not 1.1), and diminishing the imino-factor  $NH$  by 3 per cent. (since it is here an interposition factor), that is,  $-NH- = 0.755$ .

#### *The Quinone Family.*

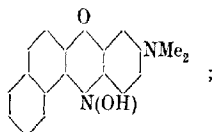
*p*-Benzoquinone in water has a band at about  $\lambda$  455 (in alcohol, about  $\lambda$  465), whence the "oxo-interposition factor" is about 1.43. This value is inconsistent with other evidence requiring a factor only slightly greater than unity. Unfortunately, the other members of the quinone family, for example,  $Ph \cdot CH_2 \cdot O \cdot$  ,  $Ph \cdot O \cdot CH_2 \cdot$  , etc., have not been examined. Possibly there are two factors for different conditions of acidity.

*The Monocyclic Acridine, Phenazine, and Phenoxazine Dyes.*  
2-Aminophenazine, as an example, may be written



and is thus seen to be  $\text{Ph}\cdot\text{N}(\text{OH})\text{C}_6\text{H}_4\text{NH}_2$  with an imino-group substituting two hydrogen atoms. This requires a factor which is *not* an interposition-factor, since in using the interposition-factors hydrogen is *not* replaced. The imino-substitution-factor is about 1.13, that is, about 3 per cent. higher than the imino-interposition-factor, as mentioned above in connexion with dicyclic azo-dyes. Hence the colour of aminophenazine is to that of aminoazobenzene as 1.03 is to 1.

There appear to be two oxo-substitution-factors, one about 1.02 for nearly neutral solutions, and the other about 1.4 for strongly acid solutions; the phenoxazines change from pink to green on acidifying. As an example, Meldola's Blue may be written as



the calculation is  $\lambda_r = 287 \times 1.20 (\text{NOH}) \times 1.135 (\text{Ph}) \times 1.15 (\text{C}_{10}\text{H}_7/\text{C}_6\text{H}_5) \times 1.02 (\text{oxo-substitution}) \times (1.19 \text{ and } 1.27) (\text{dimethyl-amino-factors}) = \lambda\lambda 550 \text{ and } 585$ . Observation gives  $\lambda\lambda 538 \text{ and } 580$ .

It is finally to be noted as a matter of great theoretical interest that the ratio  $\text{NH}/\text{CH}_2$  or  $\text{N}/\text{CH}$  or  $\text{NOH}/\text{CH}\cdot\text{OH}$  possesses the same numerical value, 1.19, in all the colour-families investigated, even in the dicyclic series of the previous paper.

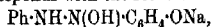
#### Summary of Monocyclic Colour-factors.

$-\text{CH}_2-$ interposed in chain .....	0.92
$-\text{NH}-$ " " " .....	1.090
$-\text{O}-$ " " " .....	1.0 and 1.4
$-\text{CH}\cdot\text{OH}-$ " " " .....	1.01
$-\text{NOH}$ " " " .....	1.200
$-\text{CH}_2-$ as second linkage to two rings .....	0.95
$-\text{NH}-$ " " " " " .....	1.13
$-\text{O}-$ " " " " " .....	1.02 and 1.4
$\text{NH}_2/\text{OH}$ auxochrome ..	1.1 (lower band), 1.18 (upper band).
$2\text{Me}_2\text{OH}$ " " " " " ..	1.19 " " 1.27 " "
naphthalene/benzene factor ..	1.15
benyl factor ..	1.135

#### Addendum.

Since this was written, I have discovered that Tuck's fundamental observation of  $\lambda 427$  for benzeneazophenol in alkaline solution (which I had used in the paper) is somewhat incorrect. The band is not broad and single as depicted by Tuck (T., 1907, **91**, diagram on page 450), but consists of *two* overlapping *narrow* bands with centres at  $\lambda\lambda 433 \text{ and } 395$ . Tuck's diagram should show a small

peak at the bottom of the curve opposite oscillation frequency 2350 (alcohol; 2450, water). Since the double band exists in the hydroxy-compounds, *two* factors are necessary there also. Probably the band  $\lambda$  433 corresponds with the formula



and the band  $\lambda$  395 with the other hydroxylated formula,



This new conception of "one formula one band" is of very great importance and will be dealt with in a subsequent communication.

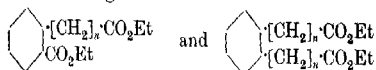
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CLXXXVI. — *Conditions of Formation of Rings attached to the o-, m-, and p-Positions of the Benzene Nucleus. Part I. The Action of Sodium on o-Phenylenediacetic Ester.*

By WILLIAM HENRY PERKIN, jun., and ALAN FRANCIS TITLEY.

THE present communication is an introduction to a series of researches which has for its principal objects, (i) the determination of the limit of size of rings which can be attached to the *o*-position in the benzene nucleus, and (ii) the investigation of the possibility of synthesising such rings in the *m*- and *p*-series. It is proposed, in the first place, to study the action of sodium on such types of *o*-esters as the following:



and then to investigate the changes which take place when the reaction is carried out with the corresponding esters of the *m*- and *p*-series.\* The present communication embodies the results of a preliminary examination of the action of sodium on *o*-phenylenediacetic ester (I).

The solution of this ester in toluene reacts readily with granulated

\* The only investigation of ring formation of this kind which appears to have been carried out previously is due to Kenner (T., 1913, 103, 613), who studied the action of sodium on 2:2'-ditolyl- $\alpha\omega'$ -dicarboxylic ester,  $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , and states that 3:5-dibenzo- $\Delta^3:5$ -cycloheptadiene-1-one-2-carboxylic ester,  $\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \\ | \\ \text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \end{array}$ , is produced to the extent of 80 per cent.

sodium at 100° with the separation of the sodium derivative of 2-hydrindone-1-carboxylic ester (II) in a yield of 90 per cent. of that theoretically possible.

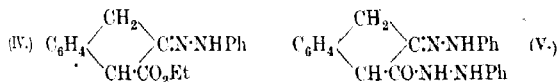


2-Hydrindone-1-carboxylic ester,  $C_6H_4 \begin{smallmatrix} \diagup CH_2 \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO \\ CHCO_2Et \end{smallmatrix}$  (IIa), obtained

from the sodium derivative by acidifying, melts at 65° and dissolves readily in sodium hydroxide with the formation of the above sodium derivative, which is rather sparingly soluble and non-hygroscopic. The alcoholic solution of the ester gives a deep purple coloration with ferric chloride and yields, with copper acetate, a crystalline copper derivative of uncertain composition. Attempts to obtain the free acid from the ester by hydrolysis under a variety of conditions have been unsuccessful. The ester is remarkably stable to alkalis and is only very slowly changed by contact with dilute methyl-alcoholic potassium hydroxide in the cold or indeed even on boiling on the water-bath. More vigorous hydrolysis with a large excess of strong alcoholic potassium hydroxide brings about a breakdown of the ring with the formation of *o*-phenylenediacetic acid together with a quantity of resinous material consisting probably of condensation products of 2-hydrindone (compare Benedict, *Annalen*, 1893, 275, 353). On the other hand, the ester readily suffers hydrolysis on boiling with dilute sulphuric acid, carbon dioxide is eliminated and an almost quantitative yield of 2-hydrin-

done,  $C_6H_4 \begin{smallmatrix} \diagup CH_2 \\ \diagdown \end{smallmatrix} CO$  (III.), obtained. The alcoholic solution of

the ester reacts at once with phenylhydrazine with the simultaneous formation of the *phenylhydrazone* (IV) and of the *phenylhydrazone phenylhydrazide* (V), which melt respectively at 176° and 187°; the *p*-nitrophenylhydrazone (m. p. 154°) has also been prepared:



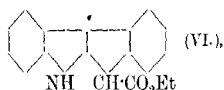
Unsuccessful attempts to obtain the corresponding pyrazolone led to the observation that the phenylhydrazone loses ammonia



on heating, and this suggested that indole formation probably takes place readily.

It was then found that the phenylhydrazone, when heated in acetic acid solution a little above  $100^{\circ}$ , is completely converted into an amorphous product, from which two crystalline substances of the empirical formula,  $C_{13}H_{15}O_2N$ , melting at  $185^{\circ}$  and  $244^{\circ}$  respectively, could be separated.

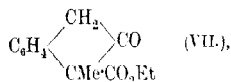
It seems probable that the substance of lower melting-point is 2:3-indeno(2:1)indolecarboxylic ester (I) (compare Armit and Robinson, this vol., p. 838),



and that the less fusible substance is derived from it by polymerisation or isomeric change. The main product of the reaction, however, consists of an uncrystallisable resin, and it is probable that the indole synthesis is complicated by the presence of the carbethoxy-group.

This suggested that the indole formation from the hydrazone of 2-hydrindone itself might repay investigation, and some experiments on this point were in progress when an account of indole synthesis from this ketone was published by Armit and Robinson (*loc. cit.*); the work was accordingly discontinued.

1-Methyl-2-hydrindone-1-carboxylic ester,



readily obtained by the action of methyl iodide on the sodium derivative of 2-hydrindone-1-carboxylic ester, is a liquid which boils at  $178-179^{\circ}/25$  mm. and yields a *semicarbazone* (m. p.  $200^{\circ}$ ) and a *p*-nitrophenylhydrazone (m. p.  $175-176^{\circ}$ ).

On alkaline hydrolysis, this ester yields *o*-phenyleneacetic- $\beta$ -propionic acid,  $C_6H_4$  (VIII), m. p.  $152^{\circ}$ , which has already been prepared by Moore and Thorpe (T., 1908, 93, 182). It was expected that acid hydrolysis would yield 1-methyl-2-hydrindone (m. p.  $63^{\circ}$ ), which has been prepared by Wallach (*Annalen*, 1904, 336, 6), but experiment showed that the ester is hydrolysed only with great difficulty by acids, the product being a red, non-acid syrup, from which no definite substance could be isolated.

## EXPERIMENTAL.

*o*-Phenylenediacetic Ester (Formula I).—The starting material used in the preparation of this ester was *o*-xylene, which was first converted into *o*-xylylene dibromide. The dibromination of *o*-xylene has been described by Perkin (T., 1888, **53**, 5) and reinvestigated by Atkinson and Thorpe (T., 1907, **91**, 1696), and a yield of about 70 per cent. of the dibromide can be obtained by direct dibromination, under the conditions recommended.

The dibromide was converted into *o*-phenylenediacetonitrile by the action of aqueous-alcoholic sodium cyanide in the manner described by Moore and Thorpe (*loc. cit.*, p. 175). It is unfortunate, in view of the difficulty of obtaining the necessary starting material—pure *o*-xylene—that the yield in this conversion is by no means quantitative, a considerable amount of oily by-products being formed. A brief study of the effect on the yield, produced by varying the proportion of alcohol in the water-alcohol mixture used as solvent, brought to light the unexpected result that the yield of nitrile is very greatly decreased by carrying out the reaction in anhydrous ethyl or methyl alcohol. The yield was indeed slightly improved by using a rather larger proportion of water in the mixture than that recommended by the above authors.

The nitrile was conveniently and quantitatively converted into *o*-phenylenediacetic ester by simultaneous hydrolysis and esterification with alcoholic hydrochloric acid.

*o*-Phenylenediacetonitrile (25 grams) was dissolved in ethyl alcohol (150 c.c.) and the solution saturated in the cold with dry hydrogen chloride gas. On boiling under reflux on the water-bath for three to four hours, a copious deposit of ammonium chloride was formed and, after cooling, this was filtered off and washed with a little alcohol. The filtrate and washings were evaporated to a small bulk under slightly diminished pressure and poured into water, when the ester separated as a dark brown, heavy oil. After extraction with ether, washing the ethereal solution with dilute sodium carbonate, and drying with potassium carbonate, the ester was fractionated under reduced pressure.

*o*-Phenylenediacetic ester boils at 173–174°/10 mm. and is a colourless, almost odourless liquid of high density (compare von Braun, *Ber.*, 1916, **49**, 2642) (Found: C = 66.8; H = 7.1. Calc., C = 67.2; H = 7.2 per cent.).

A small quantity of the ester, on hydrolysis with an excess of alcoholic potash in a sealed tube, gave a good yield of the acid, which, without recrystallisation, melted at 150° (compare Baeyer and Pape, *Ber.*, 1884, **17**, 447).

*2-Hydrindone-1-carboxylic Ester* (Formula IIa).—In preparing this ester, metallic sodium (5 grams) was granulated under toluene (75 grams), heated at 100°, and *o*-phenylenediacetic ester (24 grams), dissolved in toluene (50 grams), was added slowly from a dropping-funnel, when interaction took place at once with formation of a bulky, gelatinous sodium derivative. After all the ester had been added, the mixture was heated for a further two hours on the water-bath, and, when no further change appeared to take place, the whole was kept for twelve hours, during which a semi-solid mass of brown sodium compounds separated. About 500 grams of ice water and powdered ice were then added and the whole shaken until all the sodium derivative had dissolved. After separating from the toluene layer, the alkaline solution was extracted with ether, and the aqueous layer freed from dissolved ether by a stream of air. It was then cooled in a freezing mixture and acidified with dilute hydrochloric acid. A large quantity of a yellow oil separated, which soon became solid and could be collected by the aid of the pump and dried on porous porcelain. This crude 2-hydrindone-1-carboxylic ester is a flaky, yellow solid, readily soluble in most organic solvents except light petroleum, and the yield obtained varies between 80 and 90 per cent. It crystallises from alcohol in narrow prisms of a pale yellow colour, and has a faint but agreeable smell. By another recrystallisation from a very small quantity of ether it can be obtained quite colourless and melts sharply at 65°. This crystalline material on preservation, however, gradually becomes sticky (Found:  $C = 70.4$ ;  $H = 5.9$ .  $C_{12}H_{12}O_3$  requires  $C = 70.6$ ;  $H = 5.9$  percent.).

The alcoholic solution of the ester gives a deep purple coloration with ferric chloride and a well-defined copper salt with copper acetate. The properties of this copper salt are rather unusual. It separates as a bluish-violet, flocculent precipitate on mixing an alcoholic solution of the ester with an aqueous solution of copper acetate, and, after collecting by the aid of the pump and washing with water, alcohol, and a little ether, melts at 233°. It dissolves fairly readily in warm chloroform forming a dark, rather purplish-red solution, and when this solution is diluted with alcohol it assumes an orange colour and the salt slowly separates in small needles, which, after filtering and washing with alcohol, have a pale yellow colour. The melting point (234°) is, however, practically unchanged by this treatment.

This copper salt does not appear to possess the normal constitution  $(C_{12}H_{11}O_3)_2Cu$ , which requires  $C = 61.4$ ;  $H = 4.7$ ;  $Cu = 13.4$ , since the analysis yielded  $C = 59.0$ ;  $H = 4.5$ ;  $Cu = 15.5$  per cent.

The following molecular-weight determinations were made at different concentrations :

0.4677 Gram, 1.0059 grams, and 1.3220 grams of 2-hydrindone-carboxylic ester, respectively, dissolved in 20.8928 grams of glacial acetic acid, depressed the freezing point by  $0.418^{\circ}$ ,  $0.868^{\circ}$ , and  $1.109^{\circ}$ , whence  $M = 208$ , 216, and 222.5 (Calc. for  $C_{12}H_{12}O_3$ ,  $M = 204$ ).

The constitution of the ester is placed beyond doubt by the fact that on acid hydrolysis it is almost quantitatively converted into 2-hydrindone.

2-Hydrindone-1-carboxylic ester (10 grams) is mixed with 20 per cent. sulphuric acid (50 c.c.) and heated on the water-bath for one hour, after which steam is passed into the mixture; the ketone distils readily and solidifies in the condenser and receiver in glittering needles. By recrystallisation from dilute alcohol, long, colourless needles are obtained which melt at  $59-60^{\circ}$  (compare Moore and Thorpe, *loc. cit.*, p. 186) (Found: C = 81.5; H = 6.14. Calc., C = 81.8; H = 6.06 per cent.).

The conversion by the above method is almost quantitative, but if the hydrolysis is effected with a mixture of equal quantities of concentrated hydrochloric acid and water under the same conditions a yield of only about 10 per cent. of 2-hydrindone is obtained. The main product is a brown, non-volatile, rather resinous-looking substance, which remains in the flask after the steam distillation. This material, after collecting by the aid of the pump and washing with ether, in which it was only very slightly soluble, was recrystallised from chloroform, from which it separated in irregular rhombohedra melting at  $165-166^{\circ}$ , and proved to be anhydro-bis-2-hydrindone (compare Heusler and Schieffer, *Ber.*, 1899, **32**, 32) (Found: C = 87.6; H = 5.8. Calc., C = 87.8; H = 5.7 per cent.).

2-Hydrindonecarboxylic ester is remarkably stable to alkaline hydrolysis. It is practically unattacked by two days' standing in the cold with an excess of dilute alcoholic potash, whilst, on boiling for a short time with a strong aqueous solution of sodium hydroxide, a bulky, white precipitate of the sodium derivative is obtained, which is only moderately soluble in water and quite non-hygroscopic. On more vigorous hydrolysis with concentrated methyl-alcoholic potash, *o*-phenylenediacetic acid is obtained.

2-Hydrindonecarboxylic ester (5 grams) was boiled with a considerable excess of 15 per cent. methyl-alcoholic potash for two hours under reflux. The dark coloured solution was evaporated with water until free from methyl alcohol, concentrated to a small bulk and, when cold, filtered from the insoluble, resinous material

present. On acidifying with dilute hydrochloric acid, *o*-phenylenediacetic acid separated in yellowish-white flocks; after two recrystallisations from hot water, it melted at  $150^{\circ}$ .

*2-Hydrindone-1-carboxylic Ester Phenylhydrazone* (Formula IV).—An alcoholic solution of 2-hydrindonecarboxylic ester (2 grams) is mixed with an alcoholic solution of phenylhydrazine (1 gram), and after about a minute a voluminous, crystalline precipitate will appear. This phenylhydrazone forms long, straw-coloured needles, which dissolve fairly readily in boiling alcohol, but are almost completely insoluble in the cold solvent. It melts to a deep brown liquid at  $176\text{--}177^{\circ}$  (Found: N = 9.58.  $C_{18}H_{18}O_2N_2$  requires N = 9.52 per cent.).

The mother-liquor, on evaporation, leaves a residue of dark coloured, crystalline material, which, on recrystallisation from ethyl acetate, forms small, compact clusters of orange needles which melt with decomposition at  $188^{\circ}$  and appear to consist of the phenylhydrazone of the phenylhydrazide of 2-hydrindonecarboxylic acid (formula V) (Found: C = 73.8; H = 5.46; N = 16.0.  $C_{22}H_{20}ON_4$  requires C = 74.1; H = 5.6; N = 15.8 per cent.).

*Conversion of 2-hydrindone-1-carboxylic Ester Phenylhydrazone into 2:3-Indeno(2:1)-indolecarboxylic Ester-1* (Formula VI).—In preparing the latter substance, the phenylhydrazone (5 grams) was dissolved in glacial acetic acid (40 grams), and the mixture heated at  $105^{\circ}$ . The solution, which is at first light yellow, gradually darkens and, after an hour, develops a deep red colour with a green sheen by reflected light. When cold, it is poured into about five times its volume of water and allowed to stand, and the copious green flocculent precipitate which separates is collected, thoroughly washed with water, and dried at  $60\text{--}80^{\circ}$ . The crude product is an amorphous, bluish-green powder which commences to sinter at  $90^{\circ}$  and melts over the range  $120\text{--}140^{\circ}$ . This crude product is extracted with 50 c.c. of warm methyl alcohol, in which the main portion is insoluble and remains in the flask as a brown tar, which hardens, when quite cold, to a resin. The red methyl-alcoholic solution is poured into a large volume of ether, the clear solution washed with water until free from methyl alcohol, the ethereal solution dried with calcium chloride, and the ether distilled off, until the solution becomes cloudy. On standing, there is a gradual deposition of a nearly colourless substance, although in very small quantity, which, after filtering and washing with ether, is faintly yellow in colour, melts at  $183\text{--}185^{\circ}$ , and appears under the microscope as a mass of very small needles. A further quantity can be obtained by evaporating the ether mother-liquor to dryness, extracting with benzene, boiling the benzene solution with animal

charcoal, and adding light petroleum to the filtered solution. The material obtained in this way was less crystalline in appearance, but had a slightly higher melting point ( $185\text{--}186^\circ$ ), and there was no lowering of the melting point on mixing the two samples (Found: C = 77.6; H = 5.3; N = 5.2.  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$  requires C = 77.9; H = 5.4; N = 5.1 per cent.).

The substance dissolves in concentrated sulphuric acid with a beautiful green colour which, on standing or warming, changes to a rich blue. The indole "pine-chip" reaction gave a claret-coloured stain, much deeper than the usual bright pink coloration, but less immediate.

The methyl-alcoholic solution, if kept for some time, deposits a crystalline substance which does not dissolve on warming. This substance separates in small, colourless leaflets, which in the air gradually take on a green tinge, and melts quite sharply at  $244^\circ$ . It can also be obtained in small quantity by repeated extraction of the resinous material, insoluble in methyl alcohol (mentioned above), with benzene. The benzene solution is precipitated with light petroleum, the insoluble part redissolved in benzene and again precipitated until free from tarry matter. This higher-melting material appears to be a polymeride or isomeride of the substance of melting point  $185^\circ$ . It gives the same colour reaction with sulphuric acid, but does not give the "pine-chip" reaction (Found: C = 78.3; H = 5.3.  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$  requires C = 77.9; H = 5.4 per cent.).

The *p*-nitrophenylhydrazone of 2-hydrindone-1-carboxylic ester is readily obtained in the same manner as the phenylhydrazone (p. 1568). It forms orange needles melting at  $154^\circ$  (Found: N = 12.4.  $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}_3$  requires N = 12.4 per cent.).

It was thought possible that the *p*-nitrophenylhydrazone might undergo indole formation more easily than the phenylhydrazone and yield a cleaner product. The reverse, however, was found to be the case, and it was necessary to boil the acetic acid solution for several hours to complete the reaction. The product contained more tarry and resinous material than that obtained from the phenylhydrazone and was not further investigated.

*1-Methyl-2-hydrindone-1-carboxylic Ester* (Formula VII).—2-Hydrindonecarboxylic ester (10 grams) was converted into the sodium derivative by adding the ethereal solution to sodium, previously granulated under xylene. The sodium derivative was collected by the aid of the pump, washed with a little ether, suspended in alcohol, and methyl iodide (7.5 grams) gradually added; the mixture was then boiled under reflux for three hours on the water-bath. The bulk of the alcohol was distilled off, the residue

poured into water, the ester extracted with ether, dried, and fractionated under reduced pressure, when it boiled at 178–179°/25 mm. with slight decomposition. The distillate, which was faintly yellow in colour, had a pleasant odour and was insoluble in alkali, whilst the alcoholic solution gave no coloration with ferric chloride (Found: C = 71.0; H = 6.4.  $C_{13}H_{14}O_3$  requires C = 71.5; H = 6.4 per cent.).

The semicarbazone is readily obtained by warming the ester in methyl-alcoholic solution with semicarbazide hydrochloride and sodium acetate. It crystallises well in small, colourless needles which melt with decomposition at 200° (Found: C = 61.5; H = 6.3; N = 15.6.  $C_{14}H_{17}O_3N_3$  requires C = 61.1; H = 6.2; N = 15.3 per cent.).

The condensation product of phenylhydrazine with the ester was an oil which could not be induced to crystallise, but a *p*-nitrophenylhydrazone was obtained by shaking the ester with an aqueous solution of *p*-nitrophenylhydrazine hydrochloride to which a few drops of alcohol had been added. The oily condensation product first formed solidified on long standing and, on recrystallisation from alcohol, small, orange prisms were obtained of m.p. 175–176° (Found: N = 11.94.  $C_{19}H_{17}O_4N_3$  requires N = 11.96 per cent.).

In view of the ease with which 2-hydrindone-1-carboxylic ester undergoes acid hydrolysis, it was expected that the methyl derivative would also be fairly readily hydrolysed by acids, with the production of either 1-methyl-2-hydrindone-1-carboxylic acid or the methyl-2-hydrindone which has been previously described by Wallach (*loc. cit.*), who prepared it by the reduction of nitromethylindene. It was, however, found that the ester is remarkably resistant to acid hydrolysis. On heating for several hours with either 20 per cent. sulphuric acid or 50 per cent. hydrochloric acid and subsequently steam-distilling, practically the whole of the material was recovered unchanged, being identified by the boiling point and by conversion to the semicarbazone. By more vigorous treatment with a mixture of 1:10-sulphuric acid in glacial acetic acid, a dark red oil was obtained which, however, showed no acidic properties and decomposed completely when distilled, even under very reduced pressure. No crystalline derivative could be obtained either with semicarbazide or *p*-nitrophenylhydrazine.

Alkaline hydrolysis, however, takes place very readily, with the result that the hydrindene ring is opened and *o*-phenyleneacetic- $\beta$ -propionic acid (VIII) is produced.

The ester (5 grams) was mixed with 15 per cent. methyl-alcoholic potash (10 grams). Heat was developed, and after about five minutes a semi-solid mass of the potassium salt was formed, which

was collected, washed with a little methyl alcohol, and dissolved in water. The aqueous solution, after extraction with ether to remove traces of oil, was acidified, when the acid separated in clusters of glittering needles which, after one recrystallisation from dilute alcohol, melted at 152—153° (Found: C = 63.3; H = 5.8. Calc., C = 63.4; H = 5.8 per cent.).

One of us (A. F. T.) wishes to make acknowledgment to the Commissioners of the Exhibition of 1851 for a scholarship with the aid of which much of this work was carried out.

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## CLXXXVII.—Cevadine. Part I.

By ALEXANDER KILLEN MACBETH and ROBERT ROBINSON.

IN 1855 Merck found that the amorphous mixture of bases termed "veratrine," first isolated in 1818 by Meissner from the seeds of *Veratrum Sabadilla*, contains, along with other substances, a crystalline alkaloid which was designated cevadine. The empirical formula,  $C_{32}H_{49}O_9N$ , was established by Wright and Luff (T., 1878, 33, 338), who also effected the hydrolysis of the base by means of water in sealed tubes or with alcoholic sodium hydroxide and with production of cevine,  $C_{27}H_{43}O_8N$ , and tiglic acid.  $C_{32}H_{49}O_9N + H_2O = C_{27}H_{43}O_8N + C_5H_8O_2$ . Bossetti (Arch. Pharm., 1883, 221, 87; Jahresber., 1883, 1357) and Ahrens (Ber., 1890, 23, 2706) concluded from their further experiments that cevadine is an ester of angelic acid, whilst, on the other hand, Horst (Chem. Ztg., 1902, 26, 334) maintained the original view of Wright and Luff, since he found that ethyl tiglate was formed by the action of ethyl-alcoholic hydrochloric acid on cevadine. Under these conditions angelic acid is not transmuted into the stereoisomeric tiglic acid, and it is to be inferred that cevadine is ceving tiglate. Freund and Schwarz (Ber., 1899, 32, 800) were the first to isolate cevine in a crystalline condition. These authors heated cevadine with alcoholic potassium hydroxide, and, on cooling, a potassium compound of cevine separated as a mass of slender needles. According to Hess and Mohr (Ber., 1919, 52, [B], 1984), this derivative has the composition  $C_{27}H_{42}O_8NK.EtOK$  or  $C_{27}H_{41}O_8NK_2.EtOH$ . Cevine itself is obtained by passing a current of carbon dioxide through an aqueous solution of this salt. According to Buignet (Jahresber., 1851, 49), cevadine is optically inactive, but we have found that it



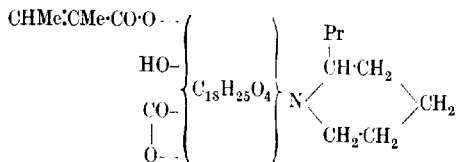
is feebly dextrorotatory, whilst cevine is levorotatory. In alcoholic solution, *o*-nitrobenzoylcevadine and di-*o*-nitrobenzoylcevine have  $[\alpha]_D^{25} = -37.5^\circ$  and  $-54.7^\circ$ , respectively, and the preparation of these substances furnishes confirmatory evidence that cevadine contains one, and cevine two, alcoholic hydroxyl groups.

In a discussion of the occurrence of optically inactive bases in plants, Hess and Weltzien (*Ber.*, 1920, **53**, [B], 122) mention the cases of cryptopine, aribine, and cevadine, now shown to occur in an active form. It is strange, in view of the exhaustive work of Perkin (*T.*, 1916, **109**, 815; 1919, **115**, 713), that it should be possible to make the statement that the constitution of cryptopine is still undetermined, whilst aribine is now known to be identical with harman, and, like cryptopine and protopine, its molecule does not contain an asymmetric carbon atom.

It is difficult to reconcile the composition of cevine and cevadine with the formation of a potassium cevine except on the assumption that this substance is the salt of an unstable hydroxy-acid produced by the opening of a lactone ring, especially since cevine exhibits no phenolic character. Attempted esterification of cevine with methyl-alcoholic hydrochloric acid resulted in amorphous products which gave low results in Zeisel estimations. Nevertheless it appears that partial esterification occurs, and in this connexion it may be remarked that cevadine gave negative results in Zeisel estimations. This is contrary to the statement of Frankforter (*Amer. Chem. J.*, 1898, **20**, 361), who considers that the cevadine molecule contains one methoxyl group. The destructive distillation of cevadine has been stated by Ahrens (*loc. cit.*) to yield, amongst other products,  $\beta$ -picoline, a little  $\beta$ -pipecoline, and isobutylene, the last possibly arising from the tiglic acid portion of the molecule. Kunz-Krause (*Pharm. Zentr.-h.*, 1898, **39**, 841) observed that when "veratrine" is evaporated with nitric acid (*d* 1.4) and the residue treated with alcoholic potassium hydroxide, the mixture turns blood-red and an odour of coniine is produced. This was confirmed by Kondakoff (*Chem. Ztg.*, 1899, **23**, 4), who attributes the odour decisively to coniine and not to  $\beta$ -picoline. By distillation of cevine with soda-lime in an atmosphere of hydrogen, we have been able to isolate in small yield a base which we believe to be *l*-coniine. The evidence is unfortunately not quite decisive (see p. 1576) owing to the fact that an authentic specimen of *l*-coniine is not available for purposes of identification,\* but we have little doubt as to the accuracy of the view we take of the nature of this decomposition product. The value of conclusions derived from

\* A comparison of the acid *l*-tertrates of synthetical *l*-coniine and of the base from cevine will subsequently be attempted.

the results of experiments at relatively high temperatures is justly discounted, but the production of such a substance as *l*-coniine scarcely falls in the category to which this criticism is applicable, and in view of the saturated character of the coniine molecule and the tertiary basic nature of cevadine it would appear to be a reasonable deduction that the coniine fragment is attached to the rest of the molecule through the nitrogen atom. The following formula for cevadine expresses this view :



On the basis of such an assumption, cevadine is a derivative of a substance,  $\text{C}_{18}\text{H}_{30}\text{O}_4$ , to which only eight hydrogen atoms must be added to produce a completely saturated compound. The occurrence of a benzene nucleus in the molecule is therefore just possible, but also improbable, since this would absorb the whole of the available unsaturation, leaving no room for the occurrence of alicyclic or oxide rings.

Experiments on the oxidation of cevine have up to the present been fruitless. When potassium permanganate in acetone solution was employed, the products were resinous acids from which nothing crystalline could be obtained. Potassium dichromate and dilute sulphuric acid gave a trace of acetone, only recognisable on account of the delicate reaction with alkaline silver mercury cyanide (Scott-Wilson, *J. Physiol.*, 1911, **42**, 444). Nitric acid produces under various conditions a yellow gum which does not crystallise. This doubtless consists partly of an acyl derivative of coniine, since it is only on this hypothesis that the survival of any coniine in the Kunz-Krause reaction is explicable.

## EXPERIMENTAL.

### *Optical Activity of Cevadine.*

Some further analyses of cevadine may be recorded (Found :  $\text{C} = 64.8, 64.9$ ;  $\text{H} = 8.3, 8.4$ ;  $\text{N} = 2.3, 2.3$ .  $\text{C}_{32}\text{H}_{49}\text{O}_9\text{N}$  requires  $\text{C} = 65.0$ ;  $\text{H} = 8.3$ ;  $\text{N} = 2.4$  per cent.).

The material used in the following determinations was recrystallised from aqueous alcohol and dried in a vacuum at  $90^\circ$  during twenty-four hours and then at  $110^\circ$  during five hours.

0.656 in 55 c.c. of ethyl alcohol in a 2-dcm. tube gave  $\alpha = +0.30^\circ$ ; whence  $[\alpha]_D^{20} = +12.5^\circ$ .

1.039 in 25 c.c. of pyridine in a 2-dcm. tube gave  $\alpha = +0.53^\circ$ ; whence  $[\alpha]_D^{20} = +6.38^\circ$ .

1.0 in 25 c.c. of acetone in a 2-dcm. tube gave  $\alpha = +0.1^\circ$ ; whence  $[\alpha]_D^{20} = +1.25^\circ$ .

*o*-Nitrobenzoylcevadine was readily obtained by adding *o*-nitrobenzoyl chloride in small quantities at a time to a suspension of cevadine in dilute aqueous potassium hydroxide, with vigorous shaking after each addition, until the odour of the chloride was no longer apparent. The cevadine gradually disappeared and its place was taken by a soft, granular precipitate. The substance was collected, washed, and dried, but could not be crystallised by treatment with solvents. It was dissolved in dilute aqueous tartaric acid and in presence of ether regenerated from the solution by means of dilute aqueous sodium hydroxide. The ethereal solution was dried by anhydrous potassium carbonate, filtered, and allowed to evaporate at the ordinary temperature. The pale yellow crystals which separated darken at  $220^\circ$  and melt with decomposition at  $236^\circ$  (Found: N = 30.8.  $C_{39}H_{52}O_{12}N_2$  requires N = 3.8 per cent.).

0.15 in 25 c.c. of ethyl alcohol in a 2-dcm. tube gave  $\alpha = -0.45^\circ$ ; whence  $[\alpha]_D^{20} = -37.5^\circ$ .

#### *Hydrolysis of Cevadine.*

In the hydrolysis of cevadine by the method of Freund and Schwarz (*loc. cit.*) it was found to be important to use pure potassium hydroxide. Commercial "veratrine" may be employed for the preparation of cevine, and the following are the details of the process. Alcohol (200 c.c.), saturated at the boiling point with potassium hydroxide, was added to a hot solution of veratrine (40 grams) in alcohol (150 c.c.), and the mixture boiled gently during half an hour. On cooling, the potassium cevine separated as a mass of slender needles, and these were collected by the aid of the pump and washed with ether. The mother-liquor, to which the ether washings were added, was concentrated to about half its bulk, and a further crop of potassium cevine was obtained, and washed with ether. The salts were separately dissolved in water and converted to cevine by passing a stream of carbon dioxide. The base was obtained in colourless prisms and proved to be identical with the substance prepared from cevadine. The yield from 150 grams of commercial veratrine was 50.5 grams of cevine from the first crop of potassium derivative and 15.0 grams from the second. 27.0 Grams of crude cevine were recovered by

evaporation of the mother-liquors from the cevine precipitated by carbon dioxide.

Cevine was crystallised from water containing a little alcohol and dried in a vacuum. This product, the composition of which is  $C_{27}H_{45}O_8N \cdot 3.5H_2O$ , was laevorotatory.

2.3278 in 50 c.c. of methyl alcohol in a 2-dcm. tube gave  $\alpha = -1.43^\circ$ ; whence  $[\alpha]_D^{25} = -15.36^\circ$ .

1.0704 in 50 c.c. of ethyl alcohol in a 2-dcm. tube gave  $\alpha = -0.75^\circ$ ; whence  $[\alpha]_D^{25} = -17.52^\circ$  (Diluted with an equal volume of water,  $[\alpha]_D^{25} = -18.68^\circ$ ).

0.203 in 25 c.c. of acetone in a 2-dcm. tube gave  $\alpha = -0.5^\circ$ ; whence  $[\alpha]_D^{25} = -30.8^\circ$ .

A solution of cevine (5 grams) in 6 per cent. methyl-alcoholic hydrochloric acid (50 c.c.) was boiled under reflux during an hour, allowed to remain for twelve hours, and then boiled during a further three hours. Silver carbonate was then added to remove hydrochloric acid, and animal charcoal to remove coloured impurities, and the liquid boiled and filtered. The methyl alcohol was removed by distillation, and the residue twice ground up with ether, which was subsequently evaporated. All possible remaining traces of methyl alcohol were then eliminated by drying the amorphous residue at  $100^\circ/10$  mm. during four hours. In a Zeisel estimation, formation of methyl iodide began at  $110^\circ$  [Found: MeO = 4.9.  $C_{27}H_{45}O_8N(OMe)$  requires OMe = 5.9 per cent.].

The washing and drying were then repeated, and in the product there was again found: MeO = 4.7 per cent.

Attempts to purify the substance by crystallisation were unsuccessful.

*Di(o-nitrobenzoyl)cevine* was prepared from cevine and *o*-nitrobenzoyl chloride by the Schotten-Baumann method. The granular product was collected, dissolved in alcohol containing a little acetic acid, and recovered by the addition of the solution to very dilute ammonia. After collecting and thoroughly washing the precipitate, it was dried in a vacuum at the ordinary temperature and then at  $100^\circ$ . The pale yellow powder is readily soluble in alcohol or ether and melts at  $175^\circ$  after softening at  $160^\circ$  (Found: C = 60.6; H = 6.0; N = 5.3.  $C_{41}H_{49}O_{14}N_3$  requires C = 61.0; H = 6.1; N = 5.2 per cent.).

0.193 Gram, dissolved in 20 c.c. of alcohol, was boiled under reflux with 70 c.c. of titanous chloride solution (18,540 c.c. equivalent to 2 grams of  $H_2$ ). Titration with iron alum then showed that 42.7 c.c. of the titanous chloride solution had been used in the reduction. Therefore a gram-molecule of di(nitrobenzoyl)cevine requires  $TiCl_3$  equivalent to 6.12  $H_2$ , and the

molecule contains two nitro-groups. Di(*o*-nitrobenzoyl)cevine is levorotatory:

0.24 in 25 c.c. of alcohol in a 2-dm. tube gave  $\alpha = -1.05^\circ$ ; whence  $[\alpha]_D^{17^\circ} = -54.7^\circ$ .

*l-Coniine (?) from Cevine.*

The Kunz-Krause-Kondakoff reaction (see p. 1572) is given by cevadine and cevine, but the base is produced in excessively minute amount. We have isolated it by steam distillation from the alkaline solution, neutralisation and concentration of the distillate, and recovery by addition of potassium hydroxide and extraction with ether. The residue, after removal of the solvent, had the powerful and characteristic odour of coniine and gave positive results in the Vitali and Stroppa (*L'Orosi*, 1900, **23**, 73) and Melzer (*Z. anal. Chem.*, 1898, **37**, 354) reactions.

Distillation of cevine with zinc dust in a stream of hydrogen also produces a base having the odour of coniine and giving a strong Vitali reaction and a picrate soluble in ether. Better results were obtained when cevine was mixed with a large excess of soda-lime and carefully distilled in a stream of hydrogen. A strongly alkaline aqueous distillate, in which was suspended drops of a reddish-brown oil, was collected. The whole was acidified with hydrochloric acid and extracted with ether several times to remove traces of neutral substances, after which the separated aqueous layer was concentrated under greatly reduced pressure. The base was set free by the addition of an excess of sodium hydroxide and distilled in steam. The distillate was just acidified with hydrochloric acid and evaporated to dryness in a vacuum. During this treatment the solution developed a pink colour changing to blue, and this behaviour is characteristic of coniine. The dry hydrochloride was extracted with absolute alcohol to separate any ammonium chloride which might be present, and the extract evaporated to dryness, mixed with concentrated aqueous sodium hydroxide, and the base again distilled in a current of steam. The distillate was thoroughly extracted with ether, and the combined extracts were dried with anhydrous sodium sulphate and evaporated to about 30 c.c. Twenty-five c.c. of the solution were employed for a determination of rotatory power (2-dm. tube), and found, on evaporation and heating at  $60^\circ$  until the weight was constant, to contain 0.962 gram of the base ( $\alpha = -1.16^\circ$ ; whence  $[\alpha]_D^{15^\circ} = -15.08^\circ$ ). This base boils at  $168-170^\circ$ , but on account of the small quantity available some superheating could not be avoided. It has the odour of coniine and gives the colour reactions

of this substance described by Vitali and Stroppa (*loc. cit.*), Gabutti (*Chem. Centr.*, 1906, II, 74), and Sanchez (*ibid.*, 1921, IV, 559). On treatment of a solution in dilute hydrochloric acid with nitrous acid, it yielded a nitroso-derivative, which was taken up in ether. After washing with sodium carbonate to remove nitrous acid, the ethereal solution was evaporated and the residue gave a strong Liebermann reaction.

The salts, except the platinichloride, could not be crystallised. The pierate, soluble in ether, melted at  $74^{\circ}$ ; the platinichloride melted at  $173-174^{\circ}$  (Found: Pt = 29.8.  $C_8H_{17}N_2, H_2PtCl_6$  requires Pt = 29.3 per cent.).

According to Löffler and Friedrich (*Ber.*, 1909, **42**, 107), *l*-coniine boils at  $166^{\circ}$  and has  $[\alpha]_D^{25} = -15.3^{\circ}$ . Its platinichloride melts at  $175^{\circ}$ .

These distillation methods are very wasteful, and further progress as well as more definite identification of the supposed *l*-coniine is dependent on the discovery of a more gentle process of decomposition, but the problem is a very difficult one.

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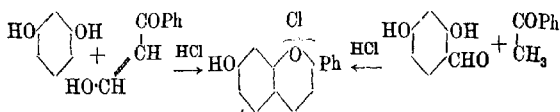
## CLXXXVIII.—A Synthesis of Pyrylium Salts of Anthocyanidin Type.

By DAVID DOIG PRATT and ROBERT ROBINSON.

AMONG the more generally applicable syntheses of anhydropyranol (pyrylium) salts there are two which are pre-eminently convenient, and in effect both depend on the condensation of a phenol, commonly a polyhydric phenol, a carboxylic acid, and a substance containing the group  $CH_2 \cdot CO$ , the last usually being a ketone. In the process developed by Bülow and his collaborators,\* a  $\beta$ -diketone or hydroxymethylene ketone is condensed with a reactive phenol by means of hydrogen chloride, whilst in that of Perkin

\* Bülow and Wagner, *Ber.*, 1901, **34**, 1195; compare also A., 1901, i, 603; 1902, i, 112, 113, 484, 354; 1903, i, 272, 357, 647, 715; 1904, i, 82, 262, 609; 1905, i, 149, 150; 1906, i, 201, 300, 598, 966.

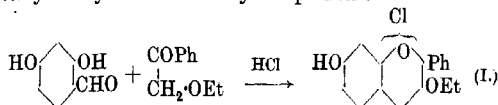
and Robinson\* and of Decker and Fellenberg an *o*-hydroxy-aldehyde is condensed with a substance containing the group  $\text{CH}_2\text{CO}$ . A typical example is illustrated below, and the relation between the two methods will be seen to be precisely that existing between the syntheses of coumarin derivatives due to Pechmann and Perkin, respectively.



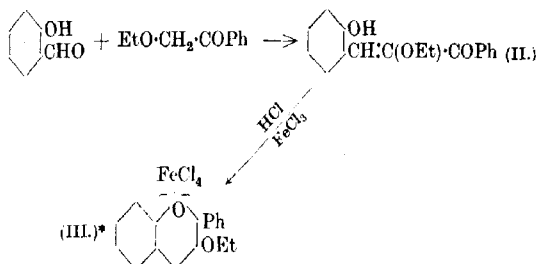
An important modification of the *o*-hydroxy-aldehyde synthesis consists in producing an *o*-hydroxystyryl ketone by condensation in alkaline solution, and subsequently converting into the pyrylium salt by the action of a strong acid. Up to the present, however, all the salts produced by applications of these reactions have been derivatives of benzopyrylium substituted in the pyrylium nucleus by various alkyl and aryl groups and, since Willstätter and his co-workers have proved in a series of brilliant investigations that the anthocyanin plant pigments are derived from 3-hydroxybenzopyrylium, it became an object to investigate conceivable extensions of the above methods to the synthesis of salts of the naturally occurring type. After some unprofitable search in other directions, we have found that derivatives of 3-hydroxybenzopyrylium salts are quite readily prepared by condensation of *o*-hydroxy-aldehydes and  $\omega$ -alkyloxy- or  $\omega$ -aryl-oxy-acetophenones. The present communication is of a preliminary character, and only a few typical examples are included. The direct condensation is exemplified by the preparation of 7-hydroxy-3-ethoxy-2-phenylbenzopyrylium chloride (I), which is

\* The first publication dealing with this reaction was a preliminary communication (Perkin and Robinson, P., 1907, **19**, 149) in which the general character of the process was clearly stated. In this paper, the salts were formulated as pyranols, but this view was abandoned in a very short time, chiefly as the result of the analysis of ferrichlorides. A more complete account of the work was recorded in 1908 (Perkin, Robinson, and Turner, T., 1908, **93**, 1085). The papers of Decker and Fellenberg (*Ber.*, 1907, **40**, 3815; *Annalen*, 1907, **356**, 281) appeared after the note of Perkin and Robinson in the *Proceedings*. The credit for the recognition of the anhydro-character of the pyranol salts is, however, due to Werner, who, in a remarkable paper on the xanthonium and thioxanthonium derivatives (*Ber.*, 1901, **34**, 3300), established the existence of the pyrylium nucleus, which he called "pyroxonium." Werner also introduced the use of the ferrichlorides which have since been so often employed for the characterisation of oxonium bases.

obtained in excellent yield when hydrogen chloride is passed into a glacial acetic acid solution of equimolecular quantities of  $\beta$ -resoreylaldehyde and  $\omega$ -ethoxyacetophenone.



3-Ethoxy-2-phenylbenzopyrylium ferrichloride (III) is, on the other hand, produced from phenyl 2-hydroxy- $\beta$ -ethoxystyryl ketone (II), which results from the condensation of salicylaldehyde and  $\omega$ -ethoxyacetophenone in methyl-alcoholic solution in presence of potassium hydroxide. The unsaturated ketone is converted to a pyrylium chloride by means of hydrogen chloride in dry ethereal solution, and the salt subsequently changed into the ferrichloride in the usual way.



The investigation is being extended in various directions such as the dealkylation of the salts and the examination of the behaviour of 3-alkyloxy- and 3-hydroxy-pyrylium salts on reduction, oxidation, and hydrolysis. In the latter connexion, Decker and Becker (*Ber.*, 1922, **55**, [B], 375) have suggested that the hydrolysis of an anthocyanidin might be expected to give rise to methylphloroglucinol. This we consider highly improbable, and in our view the products of the hydrolysis of pelargonidin, for example, should be phloroglucinol, formic acid, and *p*-hydroxybenzoylcarbinol and possibly small relative amounts of glycollic and *p*-hydroxybenzoic acids. But the benzoylcarbinols would be

\* This formula symbol is here adopted in harmony with modern conceptions of the nature of *onium* compounds and because there appears to be no reason why the supposed arrangement of valencies in the pyrylium nucleus should be indicated any more than in the similar cases of benzene and pyridine. Such expressions, moreover, at once suggest the undisputable analogies between the benzopyrylium and quinolinium salts.



likely to undergo further changes and might pass through the hydroxyphenylacetaldehydes to phenylacetic acids, mandelic acids, and condensation products.

#### EXPERIMENTAL.

*Phenyl 2-Hydroxy-β-ethoxystyryl Ketone* (Formula II).—A solution of *ω*-ethoxyacetophenone\* (16 grams), salicylaldehyde (12 grams), and potassium hydroxide (8 grams) in methyl alcohol (200 c.c.) was boiled under reflux during eight hours. The deep red solution was added to water and rendered acid by the addition of hydrochloric acid, whereby the unsaturated ketone was precipitated in silvery leaflets. The substance was collected, dried (25 grams), and crystallised from methyl alcohol, from which it separated in very pale, glistening leaflets melting at 138° (Found: C = 76.1; H = 5.8.  $C_{17}H_{16}O_3$  requires C = 76.1; H = 5.9 per cent.).

This substance is readily soluble in methyl and ethyl alcohols and in chloroform, and moderately readily soluble in ether. It dissolves in dilute aqueous potassium hydroxide to an orange-yellow solution, which is much less intensely coloured than a similar solution of salicylideneacetophenone. The solution in concentrated sulphuric acid is bright orange-red.

*3-Ethoxy-2-phenylbenzopyrylium Ferrichloride* (Formula III).—The unsaturated ketone described in the preceding section is partly converted to the corresponding pyrylium salt when it is boiled with a mixture of acetic and hydrochloric acids, but, as was found to be the case with phenyl 2-hydroxystyryl ketone (Perkin, Robinson, and Turner, *loc. cit.*), the reaction proceeds most easily in ethereal solution.

Phenyl 2-hydroxy-β-ethoxystyryl ketone (2 grams) was dissolved in pure dry ether (15 c.c.), and a stream of hydrogen chloride passed through the liquid during three hours. The solu-

\* Ethyl ethoxyacetate was prepared by condensation of ethyl chloroacetate and sodium ethoxide in ethyl-alcoholic solution (Henry, *Ber.*, 1871, 4, 706; 1873, 6, 240). The ester (12 grams) was dissolved in concentrated aqueous ammonia solution, and on evaporation ethoxyacetamide (8.5 grams), m. p. 82°, was obtained. Ethoxyacetic acids best prepared from the ester through this amide, which is treated at 90° with nitrous fumes, and the product purified by distillation. Ethoxyacetoneitrile and *ω*-ethoxyacetophenone were prepared by the excellent methods of Sommelet (*Ann. Chim. Phys.*, 1906, 9, 494, 521). It was found that the action of magnesium phenyl bromide on ethoxyacetoneitrile (22 grams) yielded ultimately 26 grams of the ethoxy-ketone boiling at 130°/15 mm. The ethoxy-derivatives were chosen for the first experiments on account of the fact that we happened to be in possession of considerable quantities of ethoxyacetamide. Corresponding methoxy-compounds are in course of investigation.

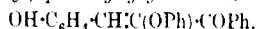
tion gradually became deep yellow and finally red, and the completion of the reaction was indicated by the complete solubility of a sample in dilute hydrochloric acid after removal of ether. Dilute hydrochloric acid was added to the reaction mixture, and after distilling off the ether the solution was boiled and filtered.

Care must be taken that the concentration of acid is sufficient to prevent hydrolysis of the oxonium salt. On the addition of an excess of ferric chloride dissolved in concentrated hydrochloric acid, the ferrichloride was precipitated as a light chocolate-brown powder. This was collected, dried in the air, and amounted to 2.5 grams. The substance crystallises well from acetic acid and is obtained in bright golden platelets melting at  $121^{\circ}$  (Found: in material dried at  $100^{\circ}$ ,  $C = 45.3$ ;  $H = 3.2$ .  $C_{17}H_{15}O_2Cl_4Fe$  requires  $C = 45.6$ ;  $H = 3.3$  per cent.).

This salt is readily soluble in hot acetic acid, but sparingly so in the cold solvent. It dissolves freely in alcohol and chloroform to yellow solutions, but is insoluble in water, and this is probably due to the coating of the crystals with a superficial layer of the related pyranol.

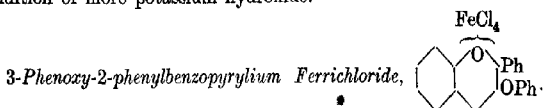
The yellow solution in concentrated sulphuric acid exhibits a pale ivy-green fluorescence. Under similar conditions, the parent substance, 2-phenylbenzopyrylium chloride, develops a blue fluorescence, and the effect of an alkyloxy-group in the 3-position is thus seen to resemble that of a similar group substituted in one of the benzene nuclei. In this connexion it may be remarked that the influence of hydroxy- and alkyloxy-groups on the colour of fluorescence in sulphuric acid solution is much less marked in the pyrone types. Thus flavone and flavonol yield pale blue and violet fluorescent solutions respectively, whilst even chrysin and k  mpferide exhibit blue fluorescences when dissolved in sulphuric acid. Many flavonol glucosides, however, develop green fluorescence under these conditions.

*Phenyl 2-Hydroxy-  -phenoxy  styryl Ketone.*



—A mixture of *m*-phenoxyacetophenone (Mohlau, *Ber.*, 1882, 15, 2497) (6 grams), salicylaldehyde (4.5 grams), and methylalcoholic potassium hydroxide (7.5 c.c. of 4 per cent.) was boiled under reflux during three hours. The red solution was diluted with water, filtered until clear, and acidified with hydrochloric acid. The precipitate was collected, washed with water, dried (5.5 grams), and crystallised from not too much methyl alcohol. Almost colourless, silvery, rhombic prisms melting at  $160^{\circ}$  were obtained (Found:  $C = 79.7$ ;  $H = 5.0$ .  $C_{21}H_{16}O_3$  requires  $C = 79.7$ ;  $H = 5.1$  per cent.).

The substance is readily soluble in alcohol, chloroform, ethyl acetate or ether, but sparingly soluble in light petroleum. It closely resembles the ethoxy-analogue previously described and dissolves in aqueous potassium hydroxide to an orange-yellow solution, from which a red oily potassium salt separates on the addition of more potassium hydroxide.



—This substance was obtained in excellent yield by the action of dry hydrogen chloride on phenyl hydroxyphenoxy-styryl ketone in ethereal solution, followed by treatment of the product with ferric chloride and hydrochloric acid exactly as described above in the case of the corresponding ethoxy-derivative. The ferrichloride crystallises from acetic acid in golden-yellow, hexagonal prisms which melt at  $149^\circ$  (Found: in material dried at  $100^\circ$ , C = 50.8; H = 3.1; Cl = 28.2.  $\text{C}_{21}\text{H}_{15}\text{O}_2\text{Cl}_4\text{Fe}$  requires C = 50.7; H = 3.0; Cl = 28.6 per cent.).

This salt is sparingly soluble in cold acetic acid, but dissolves readily in the hot solvent. It is readily soluble in methyl and ethyl alcohols and also dissolves in water to a colourless solution which doubtless contains the pyranol  $\phi$ -base. In sulphuric acid it yields a pale yellow solution which exhibits olive-green fluorescence.

*7-Hydroxy-3-ethoxy-2-phenylbenzopyrylium Chloride* (Formula I).

—A stream of hydrogen chloride was passed through a solution of  $\omega$ -ethoxyacetophenone (2 grams) and  $\beta$ -resorcyaldehyde\* (1.6

\* We prepared this substance essentially by the method of Dimroth and Zooppritz (*Ber.*, 1902, **35**, 995), but were unable to follow these authors at the stage of hydrolysis of the condensation product. Ultimately an entirely different process of hydrolysis was devised and the following are the details of the preparation, which gives good results and is easy to carry out. Phosphoryl chloride (10.2 grams) was added to a solution of resorcinol (22 grams) and formanilide (24.2 grams) in sufficient dry ether. The reaction soon commenced and was completed by gentle heating on the steam-bath during three or four hours. The mixture was allowed to remain over-night the ether was then decanted, and the yellow mass thoroughly washed with fresh ether. The salt was mixed with twenty times its weight of water and, if necessary, enough hydrochloric acid to give a reaction to Congo, and repeatedly extracted with ether on the shaking machine. In the final extraction only the liquid was saturated with salt. The combined ethereal solutions were dried with sodium sulphate, filtered, and the solvent removed. The yellow residue of resorcyaldehyde can be purified by crystallisation from water with the aid of animal charcoal, and the yield amounts to 16 grams or 60 per cent. of that theoretically possible.

grams) in glacial acetic acid (5 c.c.), when orange-red crystals began to separate after an hour, and after a further two hours filled the liquid. The salt was collected, drained as completely as possible, washed with ether, and dried (2.5 grams). The acetic acid mother-liquor contained a further amount of the same substance, and this could be isolated by the addition of ether or employed for the preparation of the derivatives described below. The chloride was found to be readily soluble in hot dilute hydrochloric acid and crystallised on cooling the orange solution in beautiful clusters of orange-red needles which decompose at  $210^{\circ}$  (Found: in material dried over sulphuric acid in a vacuum, C = 67.3; H = 4.9; Cl = 12.0.  $C_{17}H_{15}O_3Cl$  requires C = 67.4; H = 5.0; Cl = 11.7 per cent.).

It is remarkable that this salt should prove to be anhydrous, as this is a very unusual property of benzopyrylium chlorides. The substance is readily soluble in methyl or ethyl alcohol and in sulphuric acid to a yellow solution which exhibits bright apple-green fluorescence. The chloride is at once hydrolysed by water with production of a deep crimson substance, which is probably a quinonoid anhydro-base derived from the  $\gamma$ -pyranol. The substance is best obtained by the addition of sodium acetate to a solution of the chloride in dilute hydrochloric acid, and a specimen was dried and examined. It dissolves in chloroform to a red solution and is sparingly soluble in benzene, separating from a hot solution in somewhat ambiguous microcrystalline form. It dissolves in methyl alcohol to a yellow solution and is probably converted into an ether of the pyranol base. On the addition of water, a milky suspension is obtained of an almost colourless substance, and this is readily converted into the oxonium salt by the addition of a mineral acid, a clear orange solution being thus produced.

The *platinichloride* separates in small, bright red needles on the addition of platinic chloride to a hot solution of the chloride in dilute hydrochloric acid. It is very sparingly soluble in hot dilute hydrochloric acid and decomposes at  $225^{\circ}$  after darkening at  $220^{\circ}$  [Found: Pt = 20.5.  $(C_{17}H_{15}O_3Cl)_2PtCl_4$  requires Pt = 20.7 per cent.].

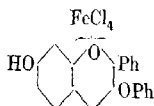
The *ferrichloride* was prepared in the usual manner from the chloride and was also obtained from the acetic acid mother-liquor resulting from the preparation of the latter, by the addition of a concentrated solution of ferric chloride in hydrochloric acid. The derivative crystallised from acetic acid in orange-red, diamond-shaped prisms (Found: C = 43.8; H = 3.2; Cl = 30.2.  $C_{17}H_{15}O_3Cl_4Fe$  requires C = 43.9; H = 3.2; Cl = 30.5 per cent.).

The substance darkens at 164° and melts at 170°. It is readily soluble in alcohol to a yellow solution, and moderately soluble in chloroform to an orange-red solution.

The *mercurichloride* crystallises from acetic acid in orange-red needles melting at 188°.

The *iodide* crystallises from methyl alcohol containing a little hydriodic acid and sulphurous acid in red, elongated, prismatic needles. On heating, it darkens at 160°, and at higher temperatures shrinks without exhibiting a definite melting point. When water is added to this salt, a perfectly clear, brilliant crimson solution is obtained. This contains the anhydro-base, doubtless in colloidal solution, and in a short time the substance separates as an intense mauve-crimson precipitate, leaving a colourless solution. The chloride also exhibits this property, but not in such a characteristic fashion. The iodide readily combines with iodine to form a *periodide* which crystallises in almost black needles. The *perchlorate* is a sparingly soluble and stable salt which crystallises from acetic acid in orange-yellow, hexagonal prisms melting at 248° with decomposition. The *picrate* crystallises from methyl alcohol in small, red prisms which darken at 205° and decompose at 215°.

7-Hydroxy-3-phenoxy-2-phenylbenzopyrylium Ferrichloride,



—*o*-Phenoxyacetophenone does not react with  $\beta$ -resorcyaldehyde with the facility which characterises the condensation of *o*-ethoxyacetophenone described above, and it was found desirable to operate under the following conditions. Hydrogen chloride was led during four hours into a solution of *o*-phenoxyacetophenone (2 grams) and  $\beta$ -resorcyaldehyde (1.4 grams) in glacial acetic acid (5 c.c.) contained in a vessel immersed in a bath at 40°. The blood-red solution was added to excess of dilute hydrochloric acid, and the mixture boiled and filtered. The addition of ferric chloride, dissolved in concentrated hydrochloric acid, to the clear orange-yellow solution caused the precipitation of the ferrichloride as an orange-yellow powder which rapidly became red. The substance was collected, dried (0.8 gram), and crystallised from glacial acetic acid. The salt is very readily soluble in the hot solvent, and separates on cooling in small, bright red tablets (Found: in material dried at 100°, C = 49.0; H = 3.0; Cl = 27.1.  $C_{21}H_{15}O_3Cl_4Fe$  requires C = 49.1; H = 2.9; Cl = 27.6 per cent.). The crystals

exhibit a beetle-green lustre and melt at  $178^{\circ}$ . The substance is readily soluble in methyl alcohol, and its solution in sulphuric acid exhibits bright apple-green fluorescence. Treatment with water hydrolyses the salt, and a deep crimson substance is produced. This dissolves in benzene to a red solution, and after concentrating to a small bulk a dark reddish-violet crust is deposited. This is apparently amorphous and melts at  $155^{\circ}$  after slight decomposition from  $150^{\circ}$ . The substance is clearly the anhydropyranol and dissolves in dilute hydrochloric acid to an orange-yellow solution, from which the ferriehloride may be regenerated.

One of us (D. D. P.) desires to express his thanks to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.

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### CLXXXIX.—*The Constitution of Polysaccharides.* *Part V. The Yield of Glucose from Cotton Cellulose.*

By JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST.

In a previous communication (Irvine and Soutar, T., 1920, **117**, 1489) it has been shown that pure glucose can be obtained from cotton cellulose by conversion of the polysaccharide into the corresponding triacetate, which is then transformed into methyl-glucoside and finally into the parent hexose. Under the conditions originally described the yield of sugar thus obtained was 85 per cent. of the theoretical amount calculated on the basis that cellulose is composed entirely of glucose units. Our further work on this subject has been directed to improving the various processes so as to account for this divergence of 15 per cent. from the theoretical value.

In essentials the experimental methods remained the same as those already described (*loc. cit.*), but a considerable improvement was effected by conducting the acetolysis of cotton cellulose as recommended by W. L. Barnett (*J. Soc. Chem. Ind.*, 1921, **40**, 8 T.). An excellent yield of uniform cellulose triacetate was thus obtained, and as no dissolved sugar was found in the aqueous washings much

tedious work was eliminated. The conversion of the triacetate into methylglucoside was varied in many ways, as described in the experimental part, but for quantitative work of this description the most accurate results were obtained by digesting small quantities of the compound with methyl alcohol containing 0.75 per cent. of hydrogen chloride. The use of an autoclave was therefore discontinued and the whole of this stage of the work was carried out in sealed tubes each containing about 4 grams of cellulose triacetate. After sixty to seventy hours at 125°, only a trace of solid matter remained, and the solution, which was faintly yellow in colour, contained the  $\alpha$ - and  $\beta$ -methylglucosides in equilibrium. The specific rotation of the liquid varied between the narrow limits +107°–108°, the concentration being calculated on the assumption that the whole of the cellulose had been transformed into methylglucoside. By means of control experiments it was shown that, under the conditions described, the equilibrium value given by the isomeric methylglucosides is  $[\alpha]_D + 107^\circ$ . Although this result might reasonably be claimed as evidence that the conversion of cellulose triacetate into methylglucoside is quantitative, our yields are now, as before, based on the weights of the glucosides obtained in pure analytical condition.

Each of the reactions involved has been carried out on numerous occasions and by independent workers. With practice and experience the yields obtained were regular, and we submit the average figures of a series of consistent experiments.

Cotton cellulose (anhydrous) .....	Parts 100	} Yield 99.5 per cent.
Cellulose triacetate .....	177	
$\alpha$ - and $\beta$ -Methylglucosides .....	114.1	} Yield 95.5 per cent.
Equivalent of glucose .....	106.0	

The overall yield from the polysaccharide to the hexose is thus 95.1 per cent. of the theoretical amount. Considering the standard of purity in which the mixed methylglucosides were isolated, there can be no further doubt that cotton cellulose is composed entirely of glucose residues (see also Monier-Williams, T., 1921, 119, 803).

Research on similar lines is being extended to the cellulose component of esparto, jute, and other fibre-bearing materials.

## EXPERIMENTAL.

*Preparation of Cellulose Triacetate.*

The cellulose employed was kindly supplied by the Research Department of Messrs. Nobels, Ltd., Ardeer, and consisted of specially purified cotton containing 10 per cent. best grade Carolina and 90 per cent. best long-staple Sakelcerides Egyptian cotton. Analysis gave :

	Per cent.
Moisture .....	6.7
Mineral matter .....	0.14
Oil .....	0.07
Soluble in 3 per cent. caustic soda .....	2.47
Copper reduction figure .....	0.37

The acetylation was carried out essentially in accordance with the method described by W. L. Barnett (*loc. cit.*), in which use is made of sulphuryl chloride as a catalyst, and the following is a description of a typical experiment. Ten grams of air-dried cotton cellulose were soaked with 50 c.c. of glacial acetic acid through which a stream of dry chlorine had been bubbled for thirty seconds. The mixture was set aside for half an hour, after which 60 c.c. of acetic anhydride were added and sulphur dioxide gas passed through the liquid for one minute. At the end of an additional hour, during which time the pasty mass was frequently stirred, the temperature was raised to 65°, and maintained at this point until the cellulose dissolved completely, giving a clear, colourless, viscous liquid. After cooling to 30°, an equal volume of chloroform was added, followed by a large excess of cold water. The chloroform was then evaporated, the mixture meanwhile being stirred continuously. During the process, the acetate separated in fine, granular particles, which were washed with several changes of water until free from acetic acid, and, after being dried at 100°, were finely powdered. Direct precipitation without the addition of chloroform gave a much bulkier precipitate, which, however, could not be powdered when dry and was much more difficult to manipulate in the subsequent experiments. Yield = 16.61 grams or 99.5 per cent. of the calculated amount of a cellulose triacetate. That no appreciable loss of material occurred during these operations was confirmed by the fact that the aqueous-acid filtrate and washings had no action on Fehling's solution, showed no optical activity and, on evaporation to dryness, gave a negligible residue. Several acetylations duplicate with that described were carried out, the yields varying between 99 and 100 per cent. of the theoretical value, allowance being made for moisture (1.5 per cent.) and



mineral matter (0.27 per cent.) [Found (corrected for mineral matter present): C = 49.82; H = 5.36.  $C_6H_7O_5(CH_3CO)_3$  requires C = 50.00; H = 5.55 per cent.].

It was considered necessary to determine the acetyl content of the specimens used in the subsequent operations. A weighed quantity of the acetate was treated for one and a half hours with a known excess of boiling aqueous sodium hydroxide, the unneutralised alkali being thereafter estimated by titration with standard sulphuric acid. Owing to the partial solubility of the "regenerated cellulose" in caustic alkali, each result had to be corrected by a control experiment in which pure cellulose was treated with sodium hydroxide under identical conditions of concentration and manipulation. A typical result is quoted:

0.4850 Gram of the acetate required 6.0 c.c. of *N*-sodium hydroxide, while 1.0 c.c. was used in the control experiment. The percentage of acetyl was therefore 44.2.  $C_6H_7O_5(CH_3CO)_3$  requires  $CH_3CO = 44.8$  per cent. This method of analysis was compared with other quantitative saponification processes and found to be satisfactory. Using *N*/2-sodium hydroxide, the limit of error is of the order  $\pm 1$  per cent. The cellulose triacetate, which had no action on Fehling's solution except on prolonged boiling, showed in chloroform solution  $[\alpha]_D = -22.3^\circ$  for  $c = 0.8092$ . The compound was stable at  $150^\circ$ , and distillation with 12 per cent. aqueous hydrochloric acid gave only negligible traces of furfural in the distillate.

*Simultaneous Hydrolysis of Cellulose Triacetate and Condensation of the Products with Methyl Alcohol.*

In carrying out the above reactions by means of acid methyl alcohol the use of an autoclave is inadvisable, as part of the "regenerated cellulose" remains unaffected and the solution becomes discoloured. Attempts were therefore made to modify the reaction so as to avoid the necessity of using a large number of sealed tubes. The results obtained are summarised, as they illustrate the narrow limits which separate success and failure.

*Method A.*—Cellulose triacetate boiled for twenty-four hours with methyl alcohol containing from 1 to 2 per cent. of hydrogen chloride. The material did not dissolve and no methylglucoside was formed.

*Method B.*—Duplicate with the above, but using methyl alcohol and chloroform in equal volumes. Product consisted of regenerated cellulose and no methylglucoside was formed.

*Method C.*—Duplicate with *B*, but using methyl alcohol (1 vol.)

and tetrachloroethane (2 vols.).  $T = 100^\circ$ . Methyl glucoside was formed, but in poor yield.

*Method D.*—Treatment of cellulose triacetate with cold methyl alcohol saturated with hydrogen chloride. A good yield of methylglucoside was obtained, but the method is unsuitable for quantitative work on a large scale.

In view of the above results the triple reaction was conducted in sealed tubes, each containing 4 grams of cellulose triacetate. A typical experiment is described.

The acetate (1 part) was heated at  $125^\circ$  for sixty to seventy hours with pure methyl alcohol (15 parts) containing 0.75 per cent. of hydrogen chloride. At the end of this period only a trace of solid remained undissolved and the liquid had assumed a golden-yellow colour. Any acid remaining after this treatment was neutralised with silver carbonate, and the filtrate decolorised, if necessary, with charcoal. Precautions were taken to recover any product remaining in the silver residues, filter papers and charcoal, and finally the whole of the neutral decolorised liquor was evaporated to a syrup under diminished pressure in a tared flask. The last traces of solvent were removed at  $100^\circ/10$  mm. by passing a current of dry air through the syrup until a constant weight was recorded. The product so obtained crystallised spontaneously, but, owing to the viscosity, solidification proceeded only slowly. Complete crystallisation was, however, effected by dissolving the syrup in a small quantity of hot alcohol and allowing the solution to remain for a few hours, after which the solvent was removed by distillation at  $60$ – $70^\circ$  under diminished pressure. The residue then remaining was crisp and uniformly crystalline. The yields and analyses quoted refer in every case to the total material isolated in this manner without any further purification. Details of two typical experiments are recorded.

	I.	II.
Weight of acetate (dry, ash-free) .....	3.990 grams	3.990 grams
Acid methyl alcohol used (0.75 per cent. hydrogen chloride) .....	60 c.c.	60 c.c.
Time at $125^\circ$ .....	50 hours	65 hours
Weight of solid remaining in sealed tube .....	0.05 gram	0.012 gram
Permanent specific rotation .....	$[\alpha]_D + 108.0^\circ$	$[\alpha]_D + 107.0^\circ$
Yield of dry crystals .....	2.570 grams	2.560 grams
Yield .....	95.6 per cent.	(calc., 2.685) 95.4 per cent.

The crystals melted between  $125$ – $150^\circ$ , a result which is in agreement with that recorded for the equilibrium mixture of  $\alpha$ - and  $\beta$ -methylglucosides (Irvine and Soutar, *loc. cit.*) and, without

recrystallisation, gave  $C = 43.12$ ;  $H = 7.19$ ;  $OMe = 15.93$  ( $C_7H_{14}O_6$  requires  $C = 43.30$ ;  $H = 7.22$ ;  $OMe = 15.95$  per cent.). No mineral matter was present and no furfural was liberated on treatment with 12 per cent. aqueous hydrochloric acid. The glucosides were therefore pure.

In acid methyl alcohol the mixed glucosides generally showed a specific rotation of the order  $[\alpha]_D + 92^\circ$  ( $c = 0.970$ ), but after further treatment at  $100^\circ$  in a sealed tube this increased to a permanent value which in different experiments varied within the extreme limits  $[\alpha]_D + 106^\circ$  to  $108^\circ$ . In most cases, however, the equilibrium rotation reported was between  $[\alpha]_D + 107^\circ$  and  $+108^\circ$ .

These figures are lower than the usually accepted value for the specific rotation of the equilibrium mixture of  $\alpha$ - and  $\beta$ -methylglucosides ( $+113^\circ$ ), but direct confirmation of the specific rotation  $+108^\circ$  for the equilibrium mixture, under the conditions of the present series of experiments, was obtained from a control experiment in which pure  $\alpha$ -methylglucoside was used. This showed an initial specific rotation of  $+158^\circ$  for  $c = 1.85$  in acid methyl alcohol (1 per cent. HCl), and after twenty hours' treatment in a sealed tube at  $100^\circ$  a constant value of  $[\alpha]_D + 107^\circ$  was obtained. The optical change observed in the products of the sealed-tube experiments thus indicates that excess of  $\beta$ -methylglucoside is initially formed. The purity of the methylglucosides was established by hydrolysing with 4 per cent. hydrochloric acid at the boiling point. The final specific rotation, when recalculated for the weight of hexose formed, was  $+52.0^\circ$  in place of  $+52.5^\circ$ , and glucose was the only sugar present in the solution. The result was confirmed by titration, using Allihn's method, when 0.9624 gram of the mixed glucosides gave, on complete hydrolysis, 0.902 gram of glucose.

#### *Isolation of a Sample of $\alpha$ -Methylglucoside.*

Recrystallisation of the mixed glucosides from absolute ethyl-alcohol gave the characteristic crystals of  $\alpha$ -methylglucoside which melted at  $165^\circ$  and showed  $[\alpha]_D + 157.8^\circ$  in aqueous solution ( $\alpha = +1.86^\circ$ ,  $l = 2$ ,  $c = 0.5892$ ). The figures for  $\alpha$ -methylglucoside are respectively  $165$ – $166^\circ$ ,  $[\alpha]_D$ , in water,  $+157.5^\circ$ . The mother-liquors from the recrystallisation now contained a considerable excess of the  $\beta$ -form, and the syrup isolated from them showed in acid methyl alcohol the specific rotation  $[\alpha]_D + 77.5^\circ$ . This material was again heated in a sealed tube with 1 per cent. acid methyl alcohol for three hours at  $100^\circ$ , when the specific rotation was found to have risen to  $+108.5$ , and at this value it remained

constant. This result confirms the views expressed that no compounds other than  $\alpha$ - and  $\beta$ -methylglucosides were present and that the conversion of cellulose triacetate into the mixed glucosides is a quantitative reaction.

The authors express their indebtedness to the Research Scheme of the Carnegie Trust for generous help received, and to Mr. Wm. Rintoul of Messrs. Nobel's Ltd., Ardeer.

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CXC.—*Preparation of o-, m-, and p-Nitrophenoxy-acetic Acids and various Nitrotoloxylacetic Acids and their Derivatives.*

By THOMAS HOSKER MINTON and HENRY STEPHEN.

THE experiments described in the following account were intended to form Part III of the investigation on coumaranones, but as the experiments in the final stages have failed to yield the desired results it was decided to present the results independently. The latter have shown that it is impossible to effect ring-closure with *o*-, *m*-, or *p*-nitrophenoxyacetic acid, using dehydrating agents, or with their acid chlorides, using aluminium chloride or copper powder, and the same remarks apply to the various nitrotoloxylacetic acids described in the following pages. This failure to bring about ring-closure is evidently connected with the ease with which the nitrophenoxy- and nitrotoloxylacetic acids undergo hydrolysis on boiling with sodium hydroxide solution, yielding the nitrophenols and nitrocresols respectively. Any attempts to dehydrate the acids with phosphoric oxide resulted in complete decomposition, and the action of aluminium chloride on the acid chlorides resulted in the formation of the nitro-phenol or -cresol. The experiments were carried out using both carbon disulphide and benzene as solvents, the acid chloride showing no tendency to react with benzene as in the ordinary Friedel-Crafts reaction.

The behaviour of the nitrophenoxyacetic acids towards alkalis recalls the similar behaviour of the methyl ethers of nitrophenols obtained by methylation of the latter, which, according to Hewitt, Johnson, and Pope (T., 1913, 103, 1626), possess the structure,  $\text{OC}_6\text{H}_4\cdot\text{NO}\cdot\text{OMe}$ , and are readily decomposed on boiling with

sodium hydroxide solution, whereas the isomeric compounds obtained by nitration of the phenol ethers are not decomposed and thus probably possess the normal structure,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . There is no evidence for concluding that the nitrophenoxyacetic acids possess the analogous structure  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , although similarity in the behaviour of the acids towards alkalis and of the acid chlorides towards condensing reagents would appear to point to such a formula. Furthermore, Hewitt, Johnson, and Pope (*loc. cit.*) examined the reactions between the sodium salts of nitrophenols and ethyl chloroacetate and found that the sodium compound of *m*-nitrophenol reacts easily, whilst *o*- and *p*-nitrophenols react with difficulty (compare Kym, *J. pr. Chem.*, 1897, [ii], 55, 113, 122). This difference was ascribed to the formation of quinonoid structure in the case of the *o*- and *p*-compounds. The present investigation has shown that *m*-nitrophenoxyacetic acid is as readily decomposed by alkali as the corresponding *o*- and *p*-acids.

#### EXPERIMENTAL.

*Preparation of o-, m-, and p-Nitrophenoxyacetic Acids.*—*o*- and *p*-Nitrophenoxyacetic acids have previously been prepared by the direct interaction of the sodium salts of the nitrophenols and chloroacetic acid, but the *m*-acid has not been prepared in this way. Hewitt, Johnson, and Pope (*loc. cit.*) describe its isolation by the hydrolysis of its ethyl ester, whilst Meyer and Duczmal (*Ber.*, 1913, 46, 3366 *et seq.*) prepared its sodium salt by the addition of chloroacetic acid to alkaline sodium *m*-nitrophenoxide and subsequent heating of the mixture for three hours on the water-bath.

The three mononitrophenoxyacetic acids have now been prepared as follows: A solution of sodium chloroacetate, prepared from 48 grams (0.5 mol.) of the acid in 60 c.c. of water, was treated with a hot solution of the nitrophenol (69 grams; 0.5 mol.) and sodium hydroxide (20 grams; 0.5 mol.) in 300 c.c. of water, and heated under reflux for ten to eleven hours. The mixture having been acidified while warm, the solid deposited on cooling was collected and purified by two crystallisations from hot water. The yields and m. p.'s of the nitrophenoxyacetic acids were: *o*-, yield 45 grams, m. p.  $156.5^\circ$ ; *m*-, yield 60 grams, m. p.  $151^\circ$  (Hewitt, Johnson, and Pope, *loc. cit.*, give  $151^\circ$ . Meyer and Duczmal, *loc. cit.*, give  $154$ – $155^\circ$ . Compare also Bischoff, *Ber.*, 1907, 40, 3143, who gives  $152$ – $153^\circ$ , and Jacobs and Heidelberger, *J. Amer. Chem. Soc.*, 1917, 39, 2191, who give  $154$ – $155^\circ$  [corr.]); *p*- yield 50 grams, m. p.  $184^\circ$  (Fritsche, *J. pr. Chem.*, 1897 [ii], 20, 290, and Pratesi, *Gazzetta*, 1891, 21, ii. 403, give  $183^\circ$ ).

The acids are fairly soluble in hot water and readily soluble in the usual organic solvents. They are not decomposed on distillation with steam or on boiling with moderately concentrated hydrochloric acid. Hot dilute sodium hydroxide solution decomposes the acids forming the sodium nitrophenoxides. In the case of *o*-nitrophenoxyacetic acid, this is not in accordance with Thate's statement (*J. pr. Chem.*, 1884 [ii], 29, 148) that the acid is stable even on boiling with concentrated potassium hydroxide solution. This has not been confirmed on a repetition of the experiment.

*o*-, *m*-, and *p*-Nitrophenoxycetyl chlorides,  $C_8H_6O_4NCl$ , were prepared by the action of thionyl chloride (1.5 mols.) on the acids (1 mol.). After gently heating the mixture for one hour, the excess of thionyl chloride was removed on the water-bath, and it was found that the acid chlorides were decomposed even by distillation under diminished pressure. They were finally obtained pure by crystallisation from dry benzene, and in each case gave good yields of large, white prisms, *m. p.* respectively 43–44.5°, 49–51°, and 83.5–84.4°. Jacobs and Heidelberger (*J. Amer. Chem. Soc.*, 1917, 39, 2424) have obtained small yields of the *o*- and *p*-acid chlorides melting at 41–42° (corr.) and 86–87° (corr.) respectively by the action of phosphorus pentachloride on the acids.

Methyl and ethyl *o*-, *m*-, and *p*-nitrophenoxycetates,  $C_9H_9O_5N$  and  $C_{10}H_{11}O_5N$  respectively, were prepared by dissolving the acid chlorides in methyl and ethyl alcohols. All except ethyl *m*-nitrophenoxycetate were obtained in the crystalline form, but this compound was isolated by pouring the reaction mixture into water and extracting with ether. After removing the ether the yellow, oily residue distilled at 187°/14 mm. (compare Hewitt, Johnson, and Pope, *loc. cit.*, who give *b. p.* 208–212°/30 mm.).

Methyl <i>o</i> -nitrophenoxycetate, white needles, <i>m. p.</i> 58°.	Duparc ( <i>Ber.</i> , 1887, 20, 1944) gives 58°.
" <i>m</i> - " " " " " " 66.5°.	
" <i>p</i> - " " " " " " 99°.	Fuchs (D.R.-P. 96492) gives 100–101°.
Ethyl <i>o</i> - " " " " leaflets, " 46–47°.	Kym ( <i>J. pr. Chem.</i> , 1897, [ii], 55, 122) gives 46–47°. Duparc ( <i>loc. cit.</i> ) gives 49.3°.
" <i>p</i> - " " " " " " 74–75°.	Kym ( <i>loc. cit.</i> ) gives 75–76°. Fuchs ( <i>loc. cit.</i> ) gives 73–74°.

*o*-, *m*-, and *p*-Nitrophenoxycetamides,  $C_8H_8O_4N_2$ .—The *o*- and *p*-compounds have been obtained by Jacobs and Heidelberger

(*loc. cit.*, p. 2421; D.R.-P. 108342) by the action of ammonia on the corresponding ethyl esters. The three amides were obtained in good yield by treating the acid chlorides with ammonia or ammonium carbonate. *o*-Nitrophenoxyacetamide forms fine, white needles, m. p. 188° (Jacobs and Heidelberger, *loc. cit.*, give 194—195°). *m*-Nitrophenoxyacetamide crystallises in pale yellow prisms, m. p. 178.5°, and the *p*-isomeride in white needles, m. p. 154—155° D.R.-P. 108342 gives 154—156°).

The amides are sparingly soluble in cold alcohol or benzene, but dissolve readily on warming. They are rapidly hydrolysed on boiling with dilute sodium hydroxide solution, and slowly on boiling with water.

*o*-, *m*-, and *p*-Nitrophenoxyacetanilides,  $C_{14}H_{12}O_4N_2$ , were prepared by treating the acid chlorides (1 mol.) with freshly distilled aniline (2 mols.). The anilides were readily hydrolysed on boiling with sodium hydroxide solution. *o*-Nitrophenoxyacetanilide forms yellow leaflets, m. p. 118.5° (Found: N = 10.18). The *m*-isomeride crystallises in fine, white needles m. p. 125° (Found: N = 10.27), and the *p*-isomeride in yellow leaflets, m. p. 170° (Kym, *loc. cit.*, gives 170—171°) ( $C_{14}H_{12}O_4N_2$  requires N = 10.30 per cent.).

4-Nitro-*m*-tolylloxyacetic acid,  $NO_2 \cdot C_6H_3Me \cdot O \cdot CH_2 \cdot CO_2H$ , was prepared from 4-nitro-*m*-cresol and chloroacetic acid by the method already described for the nitrophenoxy-acids. Unchanged nitro-cresol was removed by distillation in steam, and the acid crystallised from hot water in pale yellow needles, m. p. 157—158°. It is easily soluble in alcohol or ether, sparingly in cold benzene, but readily on warming. (Found: N = 7.01.  $C_9H_9O_5N$  requires N = 6.64 per cent.).

3-Nitro-*p*-tolylloxyacetic acid was prepared from 3-nitro-*p*-cresol and chloroacetic acid, and crystallised from hot water in pale yellow prisms, m. p. 141.5°. It is non-volatile in steam and stable to steam distillation. It is readily soluble in alcohol or ether, but only with difficulty in benzene. The yield was 50 per cent. of that theoretically possible (Found: N = 6.87.  $C_9H_9O_5N$  requires N = 6.64 per cent.).

*Derivatives of 3-Nitro-p-tolyl and 4-Nitro-m-tolyl-oxyacetic Acids.*—The acid chlorides,  $C_9H_8O_4NCl$ , were obtained by treating the acids with thionyl chloride and were crystallised from benzene. 3-Nitro-*p*-tolylloxyacetetyl chloride forms fine, white needles, m. p. 66°, and 4-nitro-*m*-tolylloxyacetetyl chloride pale yellow needles, m. p. 103.5°.

The methyl and ethyl esters,  $C_{10}H_{11}O_5N$  and  $C_{11}H_{13}O_5N$  respectively, were obtained from the acid chlorides by the method already described. Ethyl 3-nitro-*p*-tolylloxyacetate was obtained as a pale yellow oil in the same way as ethyl *m*-nitrophenoxyacetate. It

decomposed on distillation under diminished pressure, and showed signs of approaching crystallisation when cooled in ice and salt.

The *methyl* ester separated from methyl alcohol in pale yellow needles, m. p. 43°. *Methyl 4-nitro-m-tolylloxyacetate*, m. p. 69.5°, and the *ethyl* ester, m. p., 67°, crystallised from the respective alcohols in pale yellow needles.

The *amides*,  $C_9H_{10}O_4N_2$ , were obtained in good yield by treating the acid chlorides with excess of solid ammonium carbonate. *3-Nitro-p-tolylloxyacetamide* forms fine, pale yellow needles (from ethyl alcohol), m. p. 198° (Found: N = 13.52). *4-Nitro-m-tolylloxyacetamide* crystallises from ethyl alcohol in fine, pale yellow needles, m. p. 163° (Found: N = 13.31.  $C_9H_{11}O_4N_2$  requires N = 13.34 per cent.).

They are sparingly soluble in the usual organic solvents in the cold, but dissolve readily on warming, and are slowly hydrolysed on boiling with sodium hydroxide solution.

The *anilides*,  $C_{15}H_{14}O_4N_2$ , were prepared by treating the acid chlorides (1 mol.) with freshly-distilled aniline (2 mols.). *3-Nitro-p-tolylloxyacetanilide* is a white, crystalline powder (from ethyl alcohol), m. p. 116.5° (Found: N = 9.89) whilst *4-nitro-m-tolylloxyacetanilide* crystallises from ethyl alcohol in white leaflets, m. p. 202° (Found: N = 9.85.  $C_{15}H_{14}O_4N_2$  requires N = 9.79 per cent.).

These anilides are only sparingly soluble in ethyl alcohol and the usual organic solvents, and are only slowly hydrolysed on boiling with dilute sodium hydroxide solution.

Me  
 $\begin{array}{c} \diagup \quad \diagdown \\ \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \quad \diagup \\ \text{NO}_2 \end{array}$

*3-Nitro-o-tolylloxyacetic acid*, was prepared

from chloroacetic acid and 3-nitro-*o*-cresol as pale yellow needles, m. p. 129° (Found: N = 6.82.  $C_9H_9O_5N$  requires N = 6.64 per cent.). It is easily soluble in the usual organic solvents and hot water, is non-volatile, and remains undecomposed in a current of steam. The yield was not so good as in the two previous cases owing to the rapid decomposition of this acid when warmed with dilute sodium hydroxide solution.

*3-Nitro-o-tolylloxyacetyl chloride*,  $C_9H_8O_4NCl$ , was prepared by the action of thionyl chloride on the acid and obtained from benzene as a white, crystalline powder, m. p. 55°. It has a pungent odour and is readily reconverted to the acid on treatment with water.

The *methyl* and *ethyl* esters,  $C_{10}H_{11}O_5N$  and  $C_{11}H_{13}O_5N$  respectively, were obtained by treatment of the acid chloride with excess of methyl or ethyl alcohol respectively, and were recrystallised



from ethyl alcohol. The *methyl* ester forms white needles, m. p. 46.5°, and the *ethyl* ester fine, white needles, m. p. 46°.

3-Nitro-*o*-tolylloxycetamide,  $C_9H_{10}O_4N_2$ , was prepared in good yield by the action of solid ammonium carbonate on the acid chloride, and crystallised from alcohol as white crystals, m. p. 149°. It is sparingly soluble in the usual organic solvents in the cold, readily on warming, and is fairly easily hydrolysed on boiling with dilute sodium hydroxide solution (Found: N = 13.63.  $C_9H_{11}O_4N_2$  requires N = 13.34 per cent.).

3-Nitro-*o*-tolylloxycetanilide,  $C_{15}H_{14}O_4N_2$ , was obtained by the method already described, and crystallised from alcohol as white needles, m. p. 101°. It is not readily soluble in cold organic solvents, but is more soluble on warming, and is hydrolysed on boiling with sodium hydroxide solution (Found: N = 9.94.  $C_{15}H_{14}O_4N_2$  requires N = 9.79 per cent.).

2-Nitro-*p*-tolylloxycetic acid was prepared in good yield from 2-nitro-*p*-cresol, obtained by nitration of *p*-tolyl carbonate and hydrolysis of the product (compare Hollemann and Hoeflake, *Rec. trav. chim.*, 1916, **36**, 272), and chloroacetic acid. The excess of nitrocresol was removed by crystallising the product first from water and then from alcohol. The acid was obtained as pale yellow crystals, m. p. 151° (Jacobs and Heidelberger, *loc. cit.*, give 151–154° [corr.]) (Found: N = 6.91 per cent.).

It is readily soluble in the usual organic solvents and hot water, but almost insoluble in cold water, and is non-volatile and stable in a current of steam. It is much less readily decomposed by treatment with warm dilute sodium hydroxide solution than the acids previously described.

2-Nitro-*p*-tolylloxycetyl chloride,  $C_9H_8O_4NCl$ , was obtained by the action of thionyl chloride on the acid, and isolated as a white, crystalline mass, m. p. 18°.

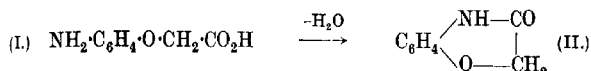
The *methyl* and *ethyl* esters,  $C_{10}H_{11}O_5N$  and  $C_{11}H_{13}O_5N$  respectively, were obtained by methods similar to those already described. They crystallise in pale yellow needles, m. p. 52° and 30°, respectively.

2-Nitro-*p*-tolylloxycetamide,  $C_9H_{10}O_4N_2$ , was prepared as already described, and crystallised from alcohol as pale yellow needles, m. p. 130°. It is soluble in the usual organic solvents, readily when warm but sparingly in the cold, and is slowly hydrolysed with hot dilute sodium hydroxide solution (Found: N = 13.59.  $C_9H_{10}O_4N_2$  requires N = 13.34 per cent.).

2-Nitro-*p*-tolylloxycetanilide,  $C_{15}H_{14}O_4N_2$ , was prepared from the acid chloride and freshly-distilled aniline, and crystallised from alcohol as pale yellow needles, m. p. 124.5°. It is readily soluble

in hot organic solvents, but almost insoluble in cold, and is hydrolysed slowly with hot dilute sodium hydroxide solution (Found: N = 10.07.  $C_{15}H_{14}O_4N_2$  requires N = 9.79 per cent.).

*Reduction of m-Nitrophenoxy- and Nitrotoloxylxy-acetic Acids.*—Thate (*J. pr. Chem.*, 1884, [ii], **29**, 148) investigated the reduction of *o*-nitrophenoxyacetic acid under various conditions, and by using sodium amalgam or iron filings with acetic acid he obtained the inner anhydride (II) of *o*-aminophenoxyacetic acid (I).



When reduction was carried out with stannous chloride and hydrochloric acid, chlorination in the nucleus took place, giving a monochloro-derivative of II. On the other hand, Howard (*Ber.*, 1897, **30**, 546) reduced *p*-nitrophenoxyacetic acid with granulated tin and glacial acetic acid and obtained *p*-acetylaminophenoxyacetic acid.

*m-Aminophenoxyacetic Acid*,  $C_8H_9O_3N$ .—*m*-Nitrophenoxyacetic acid was reduced by Howard's method (*loc. cit.*), and instead of the expected *m*-acetylaminophenoxyacetic acid gave *m*-aminophenoxyacetic acid, which crystallised as small, pale yellow needles sintering at  $204^\circ$  and gradually decomposing. It is soluble in hot water or alcohol and sparingly soluble in ether or benzene (Found: N = 8.52.  $C_8H_9O_3N$  requires N = 8.38 per cent.). The acetyl compound crystallised from hot water as a fine, yellow powder, m. p.  $167-168^\circ$  (Found: N = 6.51.  $C_{11}H_{10}O_4N$  requires N = 6.70 per cent.).

*Aminotoloxylxyacetic Acids.*—3-Nitro-*p*-tolyl-, 4-nitro-*m*-tolyl-, and 3-nitro-*o*-tolyl-oxyacetic acids were reduced by Thate's method (*loc. cit.*) using iron filings and 25 per cent. aqueous acetic acid, and in all three instances the inner anhydrides only were isolated, all of which crystallised from dilute alcohol in colourless needles.

Inner anhydride of	M. p.	N per cent.
3-Amino- <i>p</i> -tolylxyacetic acid	$209^\circ$	8.65
4-Amino- <i>m</i> -tolylxyacetic ..	193	8.69
3-Amino- <i>o</i> -tolylxyacetic ..	195	8.71
(C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> N requires N = 8.59 per cent.).		

2-Amino-*p*-tolylxyacetic acid,  $C_9H_{11}O_3N$ , was prepared by reducing the corresponding nitro-acid with stannous chloride dissolved in concentrated hydrochloric acid. It was obtained as a pale yellow, crystalline powder, soluble in boiling water, hydro-

chloric acid, or hot alcohol and almost insoluble in cold alcohol. It sintered at  $240^{\circ}$  and gradually decomposed (Found : N = 7.98.  $C_9H_{11}O_3N$  requires N = 6.28 per cent.).

The *acetyl* compound crystallised from water as white needles, m. p.  $169^{\circ}$  (Found : N = 6.5.  $C_{11}H_{13}O_4N$  requires N = 6.28 per cent.).

The authors desire to thank Mrs. E. Stephen, M.Sc., for assistance in preparing the above for publication.

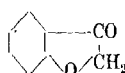
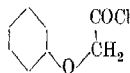
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CXCI.—*Studies in the Coumaranone Series. Part II.*  
*The Preparation of 4- and 6-Chlorocoumaran-2-ones and their Conversion into 2- and 4-Chloro-flavonols respectively, and some Derivatives of o- and p-Chlorophenoxyacetic Acids.*

By THOMAS HOSKER MINTON and HENRY STEPHEN.

It has already been shown by Higginbotham and Stephen (T., 1920, 117, 1534) that coumaranones may be obtained from phenoxy-acetic acid and its derivatives by the action of aluminium chloride on the corresponding acid chlorides, ring-formation taking place as follows :



The investigation has now been continued and extended along similar lines, and attempts have been made to prepare coumaranones containing nitro-groups and chlorine atoms in the aromatic nucleus. Only in the case of the chlorophenoxyacetic acids could the acid chlorides be converted by the above treatment into coumaranones.

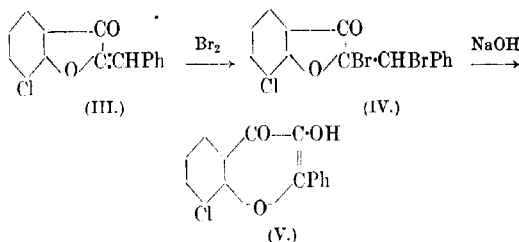
The *o*- and *p*-chlorophenoxyacetic acids required in the following experiments were readily prepared by the interaction of chloroacetic acid and the corresponding chlorophenols in alkaline solution. Numerous derivatives of the two acids and the conversion of the chlorides of the acids into 6- and 4-chlorocoumaran-2-ones

(I and II respectively), and the preparation of flavonols from the latter are described in the experimental part of the paper.



The method adopted for preparing the flavonols was similar to that described by Auwers and Müller (*Ber.*, 1908, **41**, 4233).

6-Chloro-1-benzylidenecoumaran-2-one (III) prepared from 6-chlorocoumaran-2-one and benzaldehyde, gave the dibromide (IV) on treatment with bromine, and the latter on treatment with *N*/10-sodium hydroxide solution yielded 4-chloroflavonol (V):



In a similar way 4-chlorocoumaran-2-one (II) gave 2-chloroflavonol.

#### EXPERIMENTAL.

*o*- and *p*-Chlorophenoxyacetic Acids. — The *o*-acid is stated (D.R.P. 264267) to have been prepared by the action of hot, concentrated hydrochloric acid on "oxymethylchlorophenoxyacetic acid." No description or properties of the acid are given. The *p*-acid chloride was prepared by Michael (*Amer. Chem. J.*, 1887, **9**, 216) by chlorination of phenoxyacetic acid with phosphorus pentachloride. He gives the m. p. of the acid as 151—152°. Peratoner (*Gazzetta*, 1898, **28**, i, 239) has also described the preparation of the *p*-acid by the chlorination of phenoxyacetic acid with sulphuryl chloride, and gives the m. p. as 150—151°.

The above methods of preparing the *p*-acid are open to the same objection that a certain amount of the *o*-acid is formed at the same time during the chlorination, and their separation is not likely to be an easy one. The purity of the *p*-acid, as indicated by the melting points given above, is somewhat in doubt, and the following experiments show that the pure *p*-acid melts at 155—156°.

Both acids are readily prepared by the action of chloroacetic acid on the corresponding chlorophenols in alkaline solution. The purification of the crude product was mainly dependent on the non-volatility and stability of the acids in a current of steam.

A solution of sodium chloroacetate prepared from 96 grams (1 mol.) of the acid and 53 grams (0.5 mol.) of sodium carbonate was added to a solution of 128 grams (1 mol.) of chlorophenol and 40 grams (1 mol.) of sodium hydroxide in 350 c.c. of water, and heated under a reflux for six to eight hours. The mixture was immediately acidified with 2*N*-hydrochloric or sulphuric acid, and, on cooling, a white, crystalline product was obtained which was filtered and washed with 20 c.c. of light petroleum to remove any traces of chlorophenol. The total yield was 180 grams.

*Purification of the Acids.*—The crude *o*-acid was dissolved in 3 litres of water by passing through the liquid a current of steam, which removed traces of unchanged *o*-chlorophenol. The filtered solution, on cooling, deposited fine, white needles, m. p. 145–146°. A further recrystallisation from water, alcohol, or benzene did not affect the melting point (Found : Cl = 19.18 per cent.).

Since *p*-chlorophenol is not readily volatile in steam, the crude *p*-acid was dissolved in 3.5 to 4 litres of water by passing a current of steam through the mixture. The filtered solution, on cooling, deposited large, rhombic prisms, m. p. 155–156° (Found : Cl = 19.11 per cent.\*).

*o*- and *p*-Chlorophenoxyacetyl Chlorides.—To 10 grams (1 mol.) of the acid, previously carefully dried at 80°, 15 grams (1.66 mols.) of thionyl chloride were added. Reaction took place immediately in the cold, and after a short time the mixture was warmed at 60° under reflux for one and a half hours. Excess of thionyl chloride was removed by distillation at 30°/20 mm., and the residue distilled under diminished pressure. Ten grams of each acid chloride were obtained as a pale yellow liquid, the yields being about 90 per cent. of the theoretical. Both products finally solidified to a mass of colourless needles on cooling in ice. The *o*-chloride has b. p. 136°/12 mm. and m. p. 18.4°, and the *p*-chloride, b. p. 142°/17 mm., and m. p. 18.8°. They are both soluble in carbon disulphide, benzene, or ether, and are readily hydrolysed by water to the corresponding acids. On long standing, they become coated with a red deposit, probably an oxidation product. They have pungent and characteristic odours.

*Methyl and Ethyl o- and p-Chlorophenoxyacetates.*—The esters were formed by dissolving the acid chlorides in the requisite

\* All estimations of chlorine mentioned in this work were carried out by Robertson's method (T., 1915, 107, 902).

alcohols and subsequently purifying by distillation. Methyl *o*- and *p*-chlorophenoxyacetates are colourless oils, b. p. 186–188° and 177–180° respectively. Ethyl *o*- and *p*-chlorophenoxyacetates crystallise from alcohol in white needles, m. p. 32° and 49° respectively.

*o*- and *p*-Chlorophenoxyacetamides.—Two grams of the acid chloride were mixed with excess of ammonium carbonate in a small flask, and after the first vigorous reaction had subsided, the mixture was heated on the water-bath for half an hour. After cooling, the ammonium chloride and carbonate were removed with water, and the residue crystallised from ethyl alcohol. Both amides are readily soluble in hot water, ethyl alcohol, or benzene. *o*-Chlorophenoxyacetamide forms white needles, m. p. 149.5° (Found: Cl = 19.13 per cent.). *p*-Chlorophenoxyacetamide crystallises in white needles, m. p. 153° (Found: Cl = 19.32.  $C_8H_8O_2NCl$  requires Cl = 19.11 per cent.).

*o*- and *p*-Chlorophenoxyacetanilides.—These were readily obtained by the action of aniline (2 mols.) on the acid chlorides (1 mol.) in benzene solution. After removal of the benzene by evaporation, the residue was washed with water to remove aniline hydrochloride, and purified by crystallisation from ethyl alcohol. The anilides are readily soluble in the usual organic solvents.

*o*-Chlorophenoxyacetanilide forms white needles, m. p. 121° (Found: Cl = 13.55) and the *p*-isomeride, white needles, m. p. 125° (Found: Cl = 13.67.  $C_{14}H_{12}O_2NCl$  requires Cl = 13.55 per cent.).

6-Chlorocoumaran-2-one (I).—To an ice-cold solution of 20 grams of *o*-chlorophenoxyacetyl chloride in 200 grams of carbon disulphide, 20 grams of finely powdered aluminium chloride were added slowly during two hours. The red solution and solid, after standing in the cold for several hours,\* were decomposed by concentrated hydrochloric acid and powdered ice. The oil obtained was distilled with steam for several hours until the distillate showed no reducing action with Fehling's solution. The distillate was extracted with ether, and after removing the solvent the brown residue was crystallised from ethyl alcohol as brilliant, pale yellow leaflets, m. p. 110.5°.

The coumaranone rapidly reduces Fehling's solution, gives an immediate precipitate of silver with Tollens's reagent and a purple coloration with ferric chloride solution. It gives a red solution in cold concentrated sulphuric acid or in cold sodium hydroxide solution. Crystals of the coumaranone turn yellow on exposure

\* It is essential that the mixture should not be left too long, as the yield appears to be adversely affected.

to air (Found : Cl = 21.44.  $C_8H_5O_2Cl$  requires Cl = 21.04 per cent.).

The *oxime* crystallised from dilute alcohol as small, yellow needles, m. p.  $170.5^\circ$  (Found : N = 7.50.  $C_8H_5O_2NCl$  requires N = 7.63 per cent.).

The *semicarbazone* crystallised from alcohol as yellow needles, m. p.  $228^\circ$  (Found : N = 18.23.  $C_9H_8O_2N_3Cl$  requires N = 18.63 per cent.).

The *p-nitrophenylhydrazone*, obtained as a red, crystalline powder from dilute acetic acid, melts at  $196^\circ$  (Found : N = 14.03.  $C_{14}H_{10}O_3N_3Cl$  requires N = 13.84 per cent.).

*6-Chloro-1-benzylidenecoumaran-2-one* (III) was prepared by Auwers and Müller's method (*Ber.*, 1908, **41**, 4233). A solution of 5 grams of the coumaranone and 3.2 grams of benzaldehyde in a little ethyl alcohol was warmed at  $60^\circ$  and 1–2 c.c. of concentrated hydrochloric acid were slowly added. The reaction mixture, on cooling, deposited a mass of fine, yellow needles, which were recrystallised from dilute alcohol in large yield, m. p.  $143^\circ$  (Found : Cl = 13.73.  $C_{15}H_9O_2Cl$  requires Cl = 13.82 per cent.).

*6-Chloro-1-benzylidenecoumaran-2-one dibromide* (IV) was prepared according to Auwers and Müller's method (*loc. cit.*). To a solution of 5 grams of the benzylidene compound in 10 c.c. of chloroform a solution of 3.1 grams of bromine in 10 c.c. of chloroform was added slowly. The mixture was allowed to remain overnight, and the chloroform then removed at room temperature under diminished pressure. The crude product was recrystallised from hot, glacial acetic acid as a white, crystalline powder, m. p.  $147^\circ$  (Found : total halogen = 46.51.  $C_{15}H_9O_2ClBr_2$  requires halogen = 46.90 per cent.).

*4-Chloroflavanol* (V) was prepared by the method of Auwers and Müller (*loc. cit.*), who obtained 2-methylflavanol by the action of two equivalents of 0.1 *N*-potassium hydroxide on an alcohol solution of 1-benzylidene-4-methylcoumaranone dibromide. Two grams of the dibromide already prepared were dissolved in 150 c.c. of boiling alcohol, 100 c.c. of 0.1 *N*-potassium hydroxide were slowly added, and the boiling was continued for ten minutes. On the addition of water the impure flavanol was precipitated as a brown powder, which was washed with water and crystallised from glacial acetic acid as pale yellow needles, m. p.  $187^\circ$ . The yield was 1 gram.

The flavanol is easily soluble in the usual organic solvents. Its solutions in cold concentrated sulphuric acid and sodium hydroxide are deep yellow. It does not reduce Tollens's reagent (Found : Cl = 12.28.  $C_{15}H_9O_3Cl$  requires Cl = 13.01 per cent.).

The *acetyl* compound of the flavonol was obtained (a) by the action of acetic anhydride on the flavonol, or (b) by the action of acetyl chloride on the flavonol dissolved in pyridine. The latter method gives the better yield; the acetyl compound was obtained as fine, glistening needles from methyl alcohol, m. p. 155°. It was hydrolysed on boiling for half an hour with dilute sodium hydroxide solution, the flavonol being obtained after acidifying.

4-Chlorocoumaran-2-one (II), prepared from *p*-chlorophenoxy-acetyl chloride in a similar manner to that described for 6-chlorocoumaran-2-one, was obtained in brilliant, yellow leaflets, m. p. 113.5°, having similar chemical and physical properties (Found: Cl = 21.34.  $C_8H_5O_2Cl$  requires Cl = 21.04 per cent.).

The *oxime* was obtained as fine, yellow needles from dilute alcohol, m. p. 168° (Found: N = 7.15.  $C_8H_8O_2NCl$  requires N = 7.63 per cent.).

The *semicarbazone* forms yellow crystalline powder from alcohol, m. p. 221° (Found: N = 18.36.  $C_9H_8O_2N_3Cl$  requires N = 18.63 per cent.).

The *p*-nitrophenylhydrazone, obtained as a red, crystalline powder from dilute acetic acid, melted and decomposed at 189° (Found: N = 13.56.  $C_{14}H_{10}O_3N_3Cl$  requires N = 13.84 per cent.).

4-Chloro-1-benzylidenecoumaran-2-one crystallises in fine, yellow needles from dilute alcohol, m. p. 165° (Found: Cl = 13.59.  $C_{15}H_9O_2Cl$  requires Cl = 13.82 per cent.).

4-Chloro-1-benzylidenecoumaran-2-one dibromide forms small, white prisms from glacial acetic acid, m. p. 154° (Found: total halogen = 46.73.  $C_{15}H_9O_2ClBr_2$  requires halogen = 46.90 per cent.).

2-Chloroflavonol forms yellow, glistening needles from glacial acetic acid, m. p. 162° (Found: Cl = 12.85.  $C_{15}H_9O_3Cl$  requires Cl = 13.01 per cent.).

The *acetyl* compound was obtained as fine, white needles, m. p. 140°. A small portion of it was hydrolysed to the flavonol by digestion with alcoholic sodium hydroxide, and the product melted at 161°. The properties of 2-chloroflavonol are similar to those of 4-chloroflavonol previously described.

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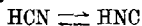
CXCH.—*Tautomerism of Dyads. Part I. Detection of Tautomeric Equilibria in Hydrocyanic Acid.*

By EDITH HILDA USHERWOOD.

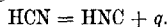
ONE of the least developed branches of the study of tautomerism is that concerned with the small but important group of organic substances termed by van Laar "dyads." Hydrocyanic acid and the cyanogen haloids are amongst the simplest of this class, and there can be no doubt that the reason why, despite the large amount of work that has been done on these substances, no definite conclusion has as yet been reached as to their precise molecular condition is that in these cases the extreme rapidity of the isomeric interchange, if it exists, is such as to render powerless those chemical and physical methods which have been employed successfully in following the attainment or detecting the existence of tautomeric equilibria in triads. New methods appear to be required, and it is the purpose of the series of papers, of which this is Part I, to develop the application of new methods to this problem.

Particular interest attaches to hydrocyanic acid. It is unnecessary to enter into the details of the evidence relating to the structure of this substance, but it may be stated broadly that, so far as chemical considerations go, the hydrolysis of hydrocyanic acid resembles that of a nitrile (Wade, *T.*, 1902, **81**, 1596), whilst its methylation with diazomethane, the mechanism of which has been investigated by Peratoner and Palazzo (*Gazzetta*, 1908, **38**, 1, 76), appears to point equally conclusively to the isonitrile formula. As regards physical evidence, Brühl has shown, on the one hand, that the refractivity of hydrocyanic acid agrees with that calculated from the nitrile formula (*Z. physikal. Chem.*, 1895, **16**, 512; compare Meyer and Hopff, *Ber.*, 1921, **54**, [B], 1709) whilst, on the other hand, Lemoult has proved that the heat of combustion agrees with the isonitrile formula (*Compt. rend.*, 1906, **143**, 902). It is solely from facts such as these that we are forced to conclude that hydrocyanic acid is neither wholly a nitrile nor wholly an isonitrile, but a mobile equilibrium mixture of these isomerides. Yet the inability of the methods hitherto employed definitely to detect the existence of an equilibrium is clearly demonstrated by the mutually contradictory conclusions to which they have led. All the circumstantial evidence appears to point to the existence (which will be assumed in what follows) of an extremely rapid interchange, the character of which approaches, perhaps more closely than in any other case, that which Lowry has aptly termed "flickering" tautomerism.

The principle underlying the method of experiment now employed depends ultimately on the fact that an equilibrium



(where  $\text{HCN}$  = formonitrile, and  $\text{HNC}$  = carbylamine, without prejudice to the possible occurrence of bivalent carbon in the latter) must alter with temperature by an amount depending on the heat,  $q$ , of the complete change



For a moderate rise of temperature this shifting of the equilibrium might be small, perhaps a few units per cent. only; but as the value of  $q$  (estimated at  $-7000$  gram-calories per gram-molecule by Lemoult (*loc. cit.*) from his own and Berthelot's thermochemical measurements on homologous nitriles and isonitriles) is enormous in comparison with the true specific heat (of the order of 10 calories), this small shifting must add very appreciably to the amount of heat which would otherwise have sufficed to raise the temperature by  $1^\circ$ . The result, therefore, is that the apparent specific heat is greater than the true specific heat, calculated according to the law of mixtures, by a certain definite fraction of the heat of reaction,  $q$ . We do not know what the specific heat of pure liquid  $\text{HCN}$  or liquid  $\text{HNC}$  should be, but in the case of the vapours the true specific heat at constant volume of either substance must be very close to 7 calories.\* It is plain, therefore, that the influence of the tautomeric equilibrium on specific heat is far greater than its influence on refractivity, or, indeed, on any property which is merely affected in accordance with the law of mixtures, and may not perhaps be very widely differentiated as regards the two individuals.

If  $x$  is the ratio of the concentration of  $\text{HCN}$  in the gas (considered as a mixture of  $\text{HCN}$  and  $\text{HNC}$ ) to the total concentration of the gas, the equilibrium constant  $K$ , is given by  $K = (1 - x)/x$ . The heat  $q$  is given by  $d \log_e K/dT = -q/RT^2$ , so that, by eliminating  $K$ , we obtain

$$dx/dT = x(1 - x)q/RT^2 \quad . \quad . \quad . \quad (i)$$

If  $dq$  is the heat evolved during a shift,  $dx$ , in the equilibrium, then  $dx$  equals  $-dq/q$ , so that

$$\delta q = -x(1 - x)q^2/RT^2 \quad . \quad . \quad . \quad (ii)$$

for a unit rise of temperature. The meaning of this equation may be best expressed by a numerical example. At  $T = 400^\circ$  ( $127^\circ \text{C.}$ ) we have, for the effective addition,  $-\delta q$ , to the true specific heat,

\* The author is aware that there are certain remarkable anomalies in the specific heat data of the simpler gases and vapours, and hopes to deal with these in a future communication, as their cause is not material to the subject of this paper.

$-\delta q = 153x(1-x)$  calories. This quantity, which may be termed the "false" specific heat, has its maximal value, 38 calories, when  $x$  and  $1-x$  are each 50 per cent.; the observed specific heat will then be 45 calories instead of 7 calories. If either  $x$  or  $1-x$  is very small, that is to say, if hydrocyanic acid is a nearly pure chemical individual, the "false" specific heat will be correspondingly small; if  $x$  or  $1-x$  were 1 per cent., then  $\delta q$  would amount only to 1.5 calories; if  $x$  or  $1-x$  were only 0.2 per cent.,  $\delta q$  would only be 0.3 calories, that is, of the order of magnitude of the amount of variation of the specific heats of different triatomic gases from the average value of 7 calories. Even in these cases, however, the method is not valueless, because the amount of variation with temperature of the false specific heat is particularly great when the quantity itself is small. Here again a numerical example may suffice in place of the general mathematical analysis. By integrating equation (i), we obtain.

$$\log_e \frac{x}{1-x} = -\frac{q}{RT} + \sigma \quad \cdot \quad \cdot \quad \text{(iii)}$$

from which the constant of integration can be eliminated by considering two temperatures, say  $T' = 400^\circ$  and  $T'' = 500^\circ$ . Two cases have to be considered. First, suppose that hydrocyanic acid is nearly pure HCN, so that  $1-x$  is small, of the order, let us say, of 1 per cent. or less. Then, from equation (iii),  $\log_e (1-x'') / (1-x') = 1.75$ , whence, by equation (ii),  $\delta q'' / \delta q' = 3.7$ . This ratio is nearly independent of the value of  $1-x$ , and represents the maximal proportional variation in the "false" specific heat when  $1-x$  tends towards zero. Hence, although the quantity of HNC might be too small to be estimated from thermal data, its existence in the equilibrated vapour should be capable of certain detection by the fact that the deviation of the observed specific heat from its asymptotic value at low temperatures (about 6.35 calories) is 3.7 times as great at  $227^\circ \text{C}$  as it is at  $127^\circ \text{C}$ , and that at other temperatures it has other easily calculated values. In the other case, which corresponds with nearly pure HNC, the limiting value, as  $x$  tends towards zero, of the ratio  $\delta q'' / \delta q'$  is 0.11, so that the variation with temperature is in the opposite sense.

It should be possible, therefore (a) to obtain an approximate measurement of the equilibrium if the scarcer constituent is present in a greater proportion than 1 per cent.; (b) if this is not the case, to detect the equilibrium, distinguishing between HCN containing a trace of HNC, and vice versa. It may be stated at once that the experiments described in this paper point definitely to the conclusion that gaseous hydrocyanic acid is a mixture consisting mainly of HCN (formonitrile) in equilibrium with a small amount, prob-

ably only a few tenths of one per cent. of the isomeric form HNC (carbylamine).

Corresponding with the deviations in the specific heat at constant volume ( $C_v$ ), there are similar deviations in the specific heat at constant pressure ( $C_p$ ), which is greater than  $C_v$  by a nearly constant amount,  $T[\delta p/\delta T]_v[\delta v/\delta T]_p = R$  approximately. Deviations in the opposite sense will, therefore, appear in the ratio  $\gamma = C_p/C_v$ , the normal value of which for a triatomic gas is close to 1.30. There seems to be a general tendency for the value of  $\gamma$  for triatomic gases to fall slightly with rising temperature, owing to causes as to the true nature of which no kind of agreement appears to have been reached. The character of the ultimate cause need not, however, concern us here, because an examination of the published data regarding such gases as carbon dioxide, sulphur dioxide, and water vapour clearly shows that in these cases the variations encountered are much smaller than that of the variation with which we have to deal in the case of hydrocyanic acid.

The equation for calculating  $\gamma = C_p/C_v$  has recently been given by Nernst ("Theoretical Chemistry," 4th ed., p. 245) in a precise form based on the very accurate equation proposed by Berthelot. In order to use Nernst's expression, however, it is essential to know the critical pressure and critical temperature. It happens that the critical data of hydrocyanic acid have not been determined, and it became necessary, therefore, to develop a generalised equation in the following way. Any equation of state can be expressed in the form

$$pv = RT[1 + p f_1(T) + p^2 f_2(T) + p^3 f_3(T) + \dots],$$

in which the successive terms represent successive orders of small quantities. On transforming van der Waals's, Clausius's or Dieterici's equation into this form, it is found that the series in powers of  $p$  is infinite, but that for pressures up to a few atmospheres, all terms after  $pf_1(T)$  are negligibly small; Berthelot's equation ceases at this term. It is clear, therefore, that, provided the function  $f_1$  be chosen suitably, there is no need to retain the higher powers of  $p$ , and we may adopt the expression

$$pv = RT[1 + pf(T)] \quad \dots \quad (iv)$$

as the general equation of state. In this expression it is supposed that the function  $f$  has been chosen suitably, for it will appear immediately that the precise form of this function is immaterial to the present discussion. Writing  $M/\rho$  in place of  $v$  and differentiating at constant temperature, we find, in the first instance,

$$\left[\frac{\delta p}{\delta \rho}\right]_T = \frac{RT}{M} \left[1 + p f(T) + \rho \frac{\delta p}{\delta \rho} f(T)\right],$$

the solution of which is

$$\left[\frac{\partial p}{\partial \rho}\right]_T = \frac{RT}{M} \left[1 + pf(T)\right]^2.$$

From this, by Reech's theorem (Partington, "Thermodynamics," p. 119) which applies to all fluids, independently of any equation of state, we obtain

$$\gamma = \left[\frac{\partial p}{\partial \rho}\right]_Q \bigg/ \left[\frac{\partial p}{\partial \rho}\right]_T = \frac{Mc^2}{RT} \cdot \frac{1}{[1 + pf(T)]^2} \quad (v)$$

Comparison of equations (iv) and (v) shows, that if, at any temperature, the observed density of a gas is greater than its theoretical value in the ratio of  $(1 + a)$  to unity, the value of  $\gamma$  for that temperature can be accurately calculated from the relation

$$\gamma = \frac{Mc^2}{RT} (1 + a)^2 \quad (vi)$$

without any knowledge as to the critical constants. Formula (vi) is the one which has been employed in the present investigation on hydrocyanic acid, and it may be hoped that it will prove to be of use in other cases.

In Table II and also in Fig. 2 will be found the values of  $\gamma$  which have been obtained by experiment compared with the values calculated by the method previously outlined. It should be noted that one cannot calculate  $\gamma$  from  $\delta q$  very accurately, because the exact value of the difference,  $C_p - C_v$ , cannot be obtained without further knowledge relating to the deviations from the gas laws.  $C_p - C_v$  must, however, be a very little greater than  $R$  ( $= 1.985$  calories), and for the purposes of an approximate calculation the value 2 calories has been assumed. Obviously, the case corresponds with the constant maximal variation of  $C_p$  with  $T$  in the region of small values of  $1 - x$ , the region characterised, for example, by the ratio  $\delta q''/\delta q' = 3.7$  for the two temperatures  $127^\circ$  and  $227^\circ$  (p. 1606). By interpolating the experimental results to these temperatures, it is easy to calculate that this ratio actually has the value 3.6\*; and that corresponding ratios for other pairs of temperatures are equally close to what they should be. It can also be calculated that  $1 - x$  is about 0.5 per cent.; but, it should be

\* This very close agreement evidently is partly accidental; for owing to the superposition of the effect discussed on p. 1607 we should have expected to obtain a higher ratio, perhaps a little more than four units. It is to be remembered, however, that  $q$  is a relatively small difference between large quantities, and may well be in error to the extent of 10 or even 20 per cent., which would more than account for the difference.

emphasised, very little reliance can be placed on any such conclusion, by reason of the fact that a considerable proportional change in  $1 - x$  would have but a slight influence on the rate of variation of  $\gamma$  with  $T$ . There can, however, be no doubt as to the broad result that the values obtained definitely point to the existence in hydrocyanic acid of an equilibrium in which formonitrile is by far the more important constituent.

#### EXPERIMENTAL.

*Preparation of Pure Hydrocyanic Acid.*—The hydrocyanic acid required for these experiments was prepared by allowing a 25 per cent. solution of pure sodium cyanide to flow into 75 per cent. sulphuric acid, maintained at  $110^\circ$ . The distillate was dried and distilled over calcium chloride, and finally over phosphoric oxide. The acid obtained in this way satisfied all the criteria for purity, and, in particular, possessed the stability, which Nef and others have found to be characteristic of the highly purified substance.

*Density of Hydrocyanic Acid.*—The vapour density of hydrocyanic acid has already been determined by Gautier (*Ann. Chim. Phys.*, 1869, [iv], 17, 119) by the Hofmann method, but the values which this author quotes exhibit certain peculiarities which render them open to suspicion. It was thought desirable, therefore, to make a new series of determinations. The Dumas method was employed, the bulbs, each of about 300 c.c. capacity, being weighed against counterpoises of the same weight and capacity and of the same quality of glass. The following corrections were applied: (i) Buoyancy corrections as affected by barometric changes, the usual scale correction being applied to all barometric readings. (ii) Hygrometric state of the atmosphere. (iii) The thermal expansion of the glass. (iv) Thermal expansion of pure water. The values obtained are summarised in the following table, and exhibited graphically in Fig 1, from which it will be seen that the density does not differ appreciably from its theoretical value, 0.932, at temperatures above  $175^\circ$ . The densities are calculated with reference to dry air under the same conditions of temperature and pressure, and the error of an individual determination is estimated at about 0.002 of a unit.

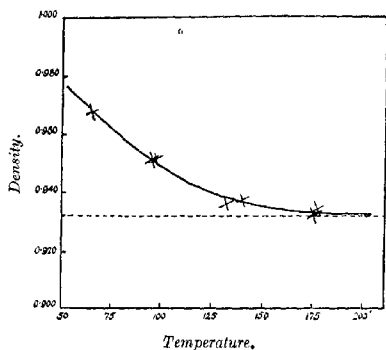
TABLE I.

Temperature	$65^\circ$	$96^\circ$	$97.5^\circ$	$132^\circ$	$140^\circ$	$175^\circ$	$177^\circ$
Density (air = 1)	0.968	0.951	0.952	0.936	0.938	0.932	0.934

*Determination of the Specific Heat Ratio.*—The method employed was that of Kundt, the tube being provided with a heating jacket in addition to the usual accessories such as inlet and outlet tubes

for the gas under investigation, an exciting rod fixed at its node to the tube, and an adjustable stop for the production of echoes. The definition of the silica dust figures was found to be dependent mainly on the completeness with which the adsorbed film of moisture was removed from the silica and from the internal surfaces of the apparatus, and on the correctness of the adjustment of the reflecting stop. By attending to these points, it was usually possible to obtain clearly marked figures at the nodes, the positions of which

FIG. 1.



were then read by means of a scale graduated in millimetres, a sliding pointer, and a mirror to prevent errors due to parallax. The temperature was kept constant by passing through the jacket the vapour of a pure liquid of the required boiling point. The pressure was that of the atmosphere. Several tubes and vibrating rods were employed, the following dimensions being typical: tube, length 126 cm., internal diameter 1.4 cm.; rod, length 94 cm., diameter 1.05 cm.

It was stated by Kundt, and appears to be generally believed, that measurements made in narrow tubes contain an appreciable error which requires correction. Rayleigh and Ramsay (*Phil. Trans.*, 1895, [A], **186**, 228), however, obtained correct results for the ratio of the specific heats of argon using tubes only 2 mm. in diameter, and there appears to be doubt as to the necessity for applying any such correction for tubes of moderate bore. In order to make certain as to this point, the apparatus was tested by determining the ratio of the specific heats of oxygen and of carbon dioxide. The value obtained for oxygen was 1.408; the mean of figures given in the literature is 1.403. The value for carbon

dioxide corrected by formula (vi) was 1.312; the mean of values recorded by previous workers, corrected, where necessary, in a similar way, is 1.306. The differences between the new values and the means obtained from the literature are not much outside the limits of experimental accuracy (estimated at 0.003), and in any case are not in the sense which suggests the existence of an appreciable error arising from the use of too narrow a tube.

The method employed in calculating the half-wave lengths may be explained by reference to an actual example. The following were the positions of some of the nodes obtained in hydrocyanic acid at 140°:

No. of node Position	1 33.30	2 40.30	3 47.20	6 68.10	7 74.90	8 81.75	9 88.70
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From these numbers the half-wave lengths,  $\lambda/2$ , were calculated by taking intervals as shown in the following table, the last column of which exhibits the errors of the individual measurements.

Nos. of nodes including interval.	No. of half- lengths in interval.	Length of interval.	Half- of wave length.	Nos. of nodes including interval.	No. of half- wave- lengths in interval.	Length of interval.	Half- of wave length.
1-6	5	34.80	6.96	2-8	6	41.45	6.91
1-7	6	41.60	6.93	2-9	7	48.40	6.91
1-8	7	48.45	6.92	3-6	3	20.90	6.97
1-9	8	55.40	6.93	3-7	4	27.70	6.93
2-6	4	27.80	6.95	3-8	5	34.55	6.91
2-7	5	34.50	6.92	3-9	6	41.50	6.92

In computing the average, each determination was accorded a value proportional to the number of half-waves in the interval.

In order to calculate the specific heat ratio of hydrocyanic acid it is necessary to know (*a*) the ratio of the specific heats of a standard gas, (*b*) the value of  $\lambda/2$  in hydrocyanic acid, (*c*) the value of  $\lambda/2$  in air, under the same conditions, (*d*) the density of hydrocyanic acid at the temperature and pressure of the experiment.

The standard gas employed was air, the specific heat ratio of which (1.403) is now known with considerable certainty.

The method of calculating  $\lambda/2$  has already been described; several experiments were carried out at each temperature. Three experiments at 180° gave the following values of  $\lambda/2$ : 7.289 cm., 7.279 cm., 7.285 cm., the extreme variation of which is less than 1 part in 700. Most of the determinations of  $\lambda/2$  agreed to within 1 part in a thousand of the mean value which was ultimately employed in computing the specific heat ratio.

The determination of  $\lambda/2$  for air was carried out in exactly the same way as for hydrocyanic acid.

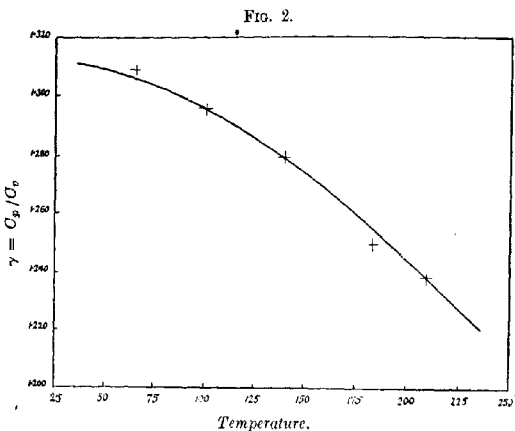


The density of hydrocyanic acid was read directly from the smoothed curve of Fig. 1.

In accordance with the equations given in the introduction to this paper, the specific heat ratio was calculated from the formula

$$\gamma_{\text{acx}} = \gamma_{\text{air}} \cdot \left( \frac{\lambda_{\text{HCN}}^2}{\lambda_{\text{air}}^2} \right)^2 \cdot 0.932.$$

The values obtained are given in the following table, the third column of which contains the theoretical figures, calculated as



noted on p. 1608, the experimental result for  $210^\circ$  being used to calculate the required numerical constants.

TABLE II.

Temperature.	$\gamma$ (observed).	$\gamma$ (calculated).	Temperature.	$\gamma$ (observed).	$\gamma$ (calculated).
$65^\circ$	1.310	1.306	$182^\circ$	1.248	1.255
$100^\circ$	1.296	1.296	$210^\circ$	1.238	(1.238)
$140^\circ$	1.279	1.279			

These results are exhibited in Fig. 2. The curve represents the theoretical function corresponding with the point ( $T = 210^\circ$ ,  $\gamma = 1.238$ ), whilst the crosses mark the values obtained by experiment.

I am greatly indebted to Dr. Ingold for valuable advice.

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CXCIII.—*Studies in Catalysis. Part XVI. The Inversion of Sucrose by Hydrogen Ion.*

By THOMAS MORAN and WILLIAM CUDMORE McCULLAGH LEWIS.

THIS reaction has already been studied by Jones and Lewis (T., 1920, 117, 1120) from the point of view of activity or thermodynamic concentration. In the investigation referred to, the activity of the catalysing ion was alone experimentally determined, it being assumed that the activity of other reactants could be identified at least approximately with concentration terms. A continuation of the investigation during the past two years by the present authors indicates, however, that this assumption is incorrect, and it has been found necessary to determine by direct or indirect means the activities of all the reactants. The reaction has been investigated in acid solution alone and also in the presence of neutral salts. The present communication deals only with the inversion process in the absence of neutral salts. The acid employed as catalyst is hydrochloric in place of the sulphuric examined in the earlier investigation. Recently Scatchard (*J. Amer. Chem. Soc.*, 1921, 43, 2387), by considering the data of Jones and Lewis mentioned above, has suggested a possible mechanism of the inversion process, but the data presented in this paper lead to conclusions which differ from those of Scatchard and also from those of Jones and Lewis.\*

## EXPERIMENTAL.

*The Activity of Hydrogen Ion in Aqueous Solutions of Sucrose and Hydrochloric Acid.*

Jones and Lewis (*loc. cit.*) found that the presence of sucrose greatly enhanced the activity of the hydrogen ion produced from the sulphuric acid. It is of interest to see if the same effect is produced when hydrochloric acid is the catalyst.

The cell employed was of the following type:—

—	0.1N-HCl	saturated	+
H <sub>2</sub> electrode	and sucrose	KCl	Normal calomel electrode

In the above cell the concentration of the hydrochloric acid was maintained constant, namely 0.1N., whilst the concentration

\* Compare also Garner and Masson, *Phil. Mag.*, 1921, [vi], 41, 484.

of the sucrose was varied from 0 to 70 grams per 100 c.c. of solution. Measurements were made at two temperatures, 25° and 35°, and the activities of the hydrogen ion calculated by means of the formulæ

$$\begin{aligned}\pi_H &= 0.2820 + 0.059 \log_{10} a_H \text{ at } 25^\circ, \\ \pi_H &= 0.2915 + 0.061 \log_{10} a_H \text{ at } 35^\circ.\end{aligned}$$

The absolute value of the normal calomel electrode was taken to be +0.56 volt at 18°. The temperature coefficient of this electrode is 0.00068 volt per degree (compare Chroustchoff and Sitnikoff, *Compt. rend.*, 1889, 108, 941), and therefore its value at 25° is 0.5648 volt and at 35° is 0.5717 volt.

The data obtained are given in Table I. It will be observed that sucrose increases the activity of hydrogen ion in the above case very markedly, even to a greater extent than was observed in the case of sulphuric acid.

*The Activity of Water in Solutions of Sucrose.*

The activity of water in solutions of sucrose may be obtained from an analysis of the data of Berkeley and Hartley (*Phil. Trans.*, 1919, [4], 218, 295) and of Berkeley and Stenhouse (*ibid.*), who have determined the values of  $\pi_0/\pi_1$  at the two temperatures 0° and 30°, where  $\pi_0$  is the vapour pressure of water and  $\pi_1$  is the vapour pressure of the aqueous solutions of sucrose. An examination of these data shows that the values of  $\pi_0/\pi_1$  corresponding with any concentration of sucrose at the temperatures 0° and 30° differ by less than 0.4 per cent. (Thus when the concentration of sucrose is 2.16 molar the difference is 0.36 per cent. This is the greatest difference, and for lower concentrations of sucrose the difference is very much less.) Hence, in calculating the activity of water at the two temperatures 25° and 35°, we may assume that the slope of the curve is the same as that observed at 30°, although the initial absolute value alters with the temperature. The relative variation in the vapour pressure with alteration in the concentration of sucrose is given in the following table.

TABLE II.

Cone. of sucrose in moles per litre.	$\pi_1$ when $\pi_0$ = 1.000.	Cone. of sucrose in moles per litre.	$\pi_1$ when $\pi_0$ = 1.000.
0.0	1.000	1.169	0.968
0.292	0.984	1.460	0.955
0.585	0.987	1.755	0.938
0.877	0.979	2.047	0.914

To obtain the absolute values for the vapour pressures at 25° and 35° it is necessary to multiply each of the above values

TABLE I.

Grams of sucrose per 100 c.c. of solution.	Temp. = 25°.				Temp. = 35°.			
	<i>E.M.F.</i> of cell observed in volt.	<i>E.M.F.</i> of cell (smoothed values).	$\pi_H$ .	$a_H$ (expressed in gram- ions per litre).	<i>E.M.F.</i> of cell observed in volt.	<i>E.M.F.</i> of cell (smoothed values).	$\pi_H$ .	$a_H$ (expressed in gram- ions per litre).
0	0.000	0.3475	0.3475	0.080	0.3462	0.3462	0.2255	0.083
10	0.292	0.3428	0.3428	0.096	0.3414	0.3414	0.2303	0.099
20	0.585	0.3381	0.3381	0.115	0.3372	0.3367	0.2350	0.118
30	0.877	0.3334	0.3334	0.139	0.3319	0.3319	0.2398	0.142
40	1.169	0.3296	0.3287	0.167	0.3270	0.3271	0.2446	0.170
50	1.460	0.3248	0.3240	0.200	0.3228	0.3223	0.2494	0.204
60	1.755	0.3188	0.3194	0.240	0.3177	0.3175	0.2542	0.245
70	2.047	0.3140	0.3147	0.288	0.3136	0.3127	0.2590	0.293

by the vapour pressure of the solvent at that temperature.  $\pi_0$  at 25° is equal to 23.69 mm., and at 35° to 42.02 mm. For the present purpose it is sufficient\* to have the relative absolute values, namely,  $\pi_0$  at 25° set equal to 1.000, and at 35° equal to  $1.000 \times 42.02/23.69$ , that is, 1.774.

*The Hydration and the Activity of Sucrose.*

On the assumption that the activity of sucrose is its concentration per free water space, several investigators, notably Porter (*Trans. Faraday Soc.*, 1917, **13**, 123), have shown that the observed osmotic pressures of sucrose solutions can be accounted for by taking hydration into account. Employing the relation

$$P_{\text{obs.}} = RTa_s = \frac{RTm}{0.018 (C_{H_2O} - nm)}$$

where  $a_s$  is the activity of the sucrose,  $m$  is the number of moles of sucrose per litre of solution,  $C_{H_2O}$  is the number of moles of water ( $M = 18$ ) per litre, of solution, and  $n$  is the degree of hydration of the sucrose, it is found that the osmotic pressures observed by Frazer and Myrick (*J. Amer. Chem. Soc.*, 1916, **38**, 1907) require  $n = 6$  (up to 20 grams of sucrose in 100 cc. of solution), this value decreasing to  $n = 4$  in agreement with Frazer and Myrick's molar fraction method of calculation. As a matter of fact, the value  $n = 4$  holds to 2 per cent. over the dilute region, and more accurately over a wide range of concentration beginning with 40 per cent. sucrose. This assumption is therefore sufficiently accurate for the present purpose.

Similar treatment of the osmotic data obtained by Berkeley and Hartley (*Phil. Trans.*, 1916, [A], **206**, 481) in the case of glucose shows that the observed osmotic pressures can be satisfactorily accounted for on the basis that  $n = 2$ .

The conclusion that over a considerable range the osmotic behaviour of sucrose and of glucose requires respectively the existence of a tetrahydrate and a dihydrate suggests naturally that two molecules of the water of hydration are attached to the oxygen atom of the ring present in each half of the sucrose molecule, the hydrated form being an oxonium compound.

*The Unimolecular Velocity Constant in Terms of Activity.*

As the polarimeter measures change of concentration,  $C$ , of sucrose with time and not change in the activity,  $a$ , it is necessary

\* The practically constant correction in the vapour pressures for the effect of the 0.1*N*-hydrochloric acid, of the order 0.2 per cent., is neglected, since only relative values are required.

to find the relation between the observed velocity constant and the velocity constant involving the activity of the sucrose. Examining this point further, the mode of expressing the unimolecular constant presents a difficulty to which attention does not seem to have been directed hitherto. The velocity may be written either as :

$$-dC_s/dt = k_a \times a_s \quad . \quad . \quad . \quad (1)$$

or

$$-da_s/dt = k_a \times a_s \quad . \quad . \quad . \quad (2)$$

In general we understand, by a velocity of chemical change, a rate of disappearance of mass of material, and this implies that velocity is identical with change in concentration. At the same time, the principle of mass action, as expressed in terms of activity, requires that the rate should be proportional to the activity, that is, equation (1) seems to be the more correct way of expressing the rate. On the other hand, the polarimeter method leads to a velocity constant,  $k_{\text{obs.}}$  which is necessarily defined by

$$-dC_s/dt = k_{\text{obs.}} \times C_s \quad . \quad . \quad . \quad (3)$$

Combining equations (1) and (3), we have

$$k_a \times a_s = k_{\text{obs.}} \times C_s$$

$$\text{or } k_a = k_{\text{obs.}} \times C_s/a_s = k_{\text{obs.}} \times C_{\text{uncorr.}}/C_{\text{corr.}} = k_{\text{obs.}} \times (V-v)/V$$

where  $V$  is the volume of the solution and  $v$  is the volume occupied by the hydrated sucrose. Hence  $(V-v)/V$  is the volume of "free" water per c.c. of solution. Consequently,

$$k_a = k_{\text{obs.}} \times 0.018 \times (\text{Conc. of free water}) \quad . \quad (4)$$

Table IV contains the values of  $k_{\text{obs.}}$  at 25° and 35° determined with great care in this laboratory by Miss D. E. Merriman, M.Sc., together with the values of  $k_a$  calculated by means of equation (4). 0.1N-Hydrochloric acid is employed as catalyst, and the values of  $k_{\text{obs.}}$  are expressed in  $\text{secs.}^{-1}$ , with logarithms to the base  $e$ .

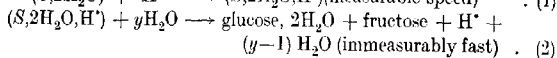
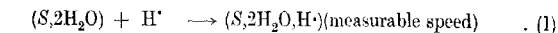
TABLE III.

Initial conc. of sucrose in moles per litre of soln.	Conc. of free water per litre of soln.	$k_{\text{obs.}} \times 10^5$ at 25°.	$k_a \times 10^5$ at 25°.	$k_{\text{obs.}} \times 10^5$ at 35°.	$k_a \times 10^5$ at 35°.
0.000	55.55	1.21	1.21	5.00	5.00
0.292	50.78	1.36	1.24	5.65	5.165
0.585	46.11	1.52	1.26	6.33	5.25
0.877	41.48	1.68	1.26	7.00	5.23
1.169	36.94	1.83	1.23	7.66	5.09
1.460	32.25	1.99	1.16	8.33	4.84
1.755	27.57	2.15	1.07	9.07	4.50
2.047	22.75	2.30	0.94	9.66	3.96

It will be observed that the values of  $k_a$  at both temperatures go through a maximum.

*The Mechanism of the Inversion Process.*

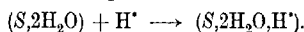
In suggesting a mechanism of the inversion process it is essential to take into consideration the structural organic side of the problem, as well as the calculation of satisfactory critical increments for the reactants from the calculated velocity constants. Armstrong ("The Simple Carbohydrates and the Glucosides," p. 133) considers the inversion process to originate at the oxygen ring in the fructose side of the sucrose molecule, which would lead us to believe that either a totally unhydrated sucrose molecule or one with no water of hydration attached to the fructose portion should be the reactant. On the latter basis, the mechanism of inversion would consist essentially of two consecutive processes. In the first place, a molecule of sucrose dihydrate combines with an unhydrated hydrogen ion giving an additive product which, however, has only a fugitive existence, since one or more of the contiguous water molecules immediately reacts with this complex to give glucose dihydrate, fructose, and hydrogen ion. The above mechanism may be expressed by the following equations, in which  $S$  stands for an unhydrated sucrose molecule and  $y$  denotes an undetermined number of water molecules:



It will be observed that the process here considered differs from the mechanism suggested by Jones and Lewis (*loc. cit.*) in that, on the earliest view, the formation of the complex ion was regarded as occurring immeasurably fast and the actual existence of a complex ion was postulated, whilst on the present basis this is no longer assumed to be true, the measurable process being the reaction between an unhydrated hydrogen ion and sucrose dihydrate.

The reaction expressed in equation (1), being the slow one, determines the rate of inversion, and moreover, since it is bimolecular, we should expect the viscosity, which changes greatly in the system under consideration in view of the wide range of sucrose concentration employed, to play an important rôle. The detailed treatment given below indicates that this is the case, and furthermore that the power to which the viscosity has to be raised to account quantitatively for the velocity constant is identical, within the limits of error, with that calculated for the effect of viscosity on the mobility of the hydrogen ion as given by conductivity measurements. Of the two reactants sucrose dihydrate and the unhydrated hydrogen ion, the latter is the fast moving ion and it is this which

will in the main be affected by alteration in viscosity, since we can regard the sucrose molecule as practically stationary. Let us suppose that the viscosity factor for this ion is  $\eta^x$ , that is, the speed of the diffusion of the hydrogen ion varies inversely as the viscosity ( $\eta$ ) of the solution raised to the power  $x$ , then from the equation



it follows that

$$\text{rate of inversion} = k_{bi} \times a_{S, 2H_2O} \times \frac{a_{H^+}}{\eta^x},$$

where  $a_{S, 2H_2O}$  denotes the activity of sucrose dihydrate, and  $a_{H^+}$  denotes the activity of unhydrated hydrogen ion. But from the direct inversion measurements themselves, we have already shown that

$$\text{rate of inversion} = k_a \times a_{S, 4H_2O},$$

where the values of  $k_a$  are given in Table IV, and  $a_{S, 4H_2O}$  is the activity of the sucrose which has been shown probably to exist almost entirely in the form of the tetrahydrate.

Denoting by  $K$  the equilibrium constant between sucrose dihydrate and sucrose tetrahydrate, that is

$$K = a_{S, 4H_2O} / a_{S, 2H_2O} \times a_{H_2O}^2$$

it follows that

$$\text{rate of inversion} = k_{bi} \times a_{S, 4H_2O} / (K \times a_{H_2O}^2) \times a_{H^+} / \eta^x$$

or

$$k_{bi} = (k_a \times A_{H_2O}^2 \times \eta^x \times K) / a_{H^+}.$$

The best values of  $x$ , determined by the method of least squares, which give the best constant for  $k_{bi}$  at 25° and 35° are 0.52 and 0.55 respectively. The results are shown in Tables V and VI. The absolute values of the viscosity at 25° and 35° were determined by Powell (T., 1914, 105, 3).

TABLE IV.

N/10-Hydrochloric acid as catalyst. Temperature = 25°.

Grams of sucrose per 100 c.c. of solution.	$k_a \times 10^3$ .	$a_{H^+}$ .	$a_{H_2O}$ .	$\eta$ .	$\eta^{0.52}$ .	$k \times 10^6 \dots \frac{k_{bi} \times 10^4}{K}$
						$k_a \times a_{H_2O}^2 \times \eta^{0.52} \times 10^6$ .
0	1.21	0.080	1.000	0.00904	0.0865	13.1
10	1.24	0.096	0.994	0.01187	0.1000	12.8
20	1.26	0.115	0.987	0.01622	0.1172	12.5
30	1.26	0.139	0.979	0.02366	0.1428	12.4
40	1.23	0.167	0.968	0.03683	0.1797	12.4
50	1.16	0.200	0.955	0.06171	0.2348	12.4
60	1.07	0.240	0.938	0.1149	0.3246	12.7
70	0.94	0.288	0.914	0.2335	0.4694	12.8



TABLE V.

*N*/10-Hydrochloric acid as catalyst. Temperature = 35°.

Grams of sucrose per 100 c.c. of solution.	$k_a \times 10^5$ .	$a_H$ .	$a_{H_2O}$ .	$\eta$ .	$\eta^{0.55}$ .	$k \times 10^5 = \frac{k_H}{K} \times 10^5 =$
						$\frac{k_a \times a_{H_2O}^2 \times \eta^{0.55}}{a_H} \times 10$ .
0	5.00	0.083	1.774	0.00726	0.0867	12.5
10	5.165	0.099	1.764	0.00932	0.0763	12.4
20	5.25	0.118	1.751	0.01270	0.0906	12.3
30	5.23	0.142	1.737	0.01795	0.1096	12.2
40	5.09	0.170	1.718	0.02713	0.1375	12.2
50	4.84	0.204	1.694	0.04321	0.1777	12.1
60	4.50	0.245	1.664	0.07781	0.2455	12.5
70	3.96	0.293	1.622	0.1460	0.3471	12.3

At both temperatures the values of  $k_H/K$  are satisfactory. The fact that the index of the viscosity correction differs from unity follows from the inapplicability of Stokes's law in the case of ions. MacInnes (*J. Amer. Chem. Soc.*, 1921, **43**, 1217) shows that the correction  $\eta^{0.7}$  in the case of chlorine ion holds for all dilutions of this ion, whilst Green (T., 1908, **93**, 2049), from determinations of the conductivity of hydrochloric acid in the presence of sucrose, finds the correction for this acid to be  $\eta^{0.55}$  at infinite dilution. On the other hand, unpublished work by Mr. A. J. Kieran in this laboratory shows that the viscosity correction in the latter case is  $\eta^{0.67}$ . Employing these facts, it is readily shown that for hydrogen ion alone, using the observations of MacInnes and Green, the index of the viscosity factor should be 0.52 at 25°, whilst combining the conclusions of MacInnes and Kieran the index should be 0.55 at 25°. In view of this, the value 0.52 obtained from the examination of the kinetics of the inversion process at 25° is very significant. It constitutes considerable evidence in favour of the mechanism outlined above.

In connexion with the activity of water, a relatively minor point arises as to the exact manner of expressing this quantity. In accordance with the usual mode of expression the activity has been identified in tables V and VI with the vapour pressure. In view, however, of the general concept of activity as a modified concentration term, it would seem more correct to employ the concentration,  $C$ , of saturated vapour, instead of the pressure, the vapour being regarded as a perfect gas (the variation of  $C$  with temperature is governed by the internal latent heat of vaporisation of the solvent, whereas  $p$  is determined by a larger quantity, namely, the observed latent heat). Employing  $C$  instead of  $p$ , the

ratio of  $k$  at  $35^\circ$  to  $k$  at  $25^\circ$  (where  $k = k_{bi}/K$ ) will be decreased by the square of the ratio of the absolute temperatures, that is, by  $(298/308)^2 = 0.936$ , whence the critical increment,  $E_k$ , as defined by the equation

$$d \log k/dT = E_k/RT^2,$$

is found to be 40,200 calories.

*The Critical Increment of the Inversion Process.*

It has been shown that

$$k_{bi} = (k_a \times a_{H_2O}^2 \times \eta^r \times K)/a_H = k \times K,$$

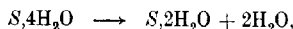
where  $k$  is the constant given in the final column of the preceding tables V and VI. It follows that

$$d \log k_{bi}/dT = d \log k/dT + d \log K/dT.$$

Expressing the activity of water in terms of the concentration of saturated vapour, it has been shown above that

$$d \log k/dT = 40,200/RT^2.$$

Denoting by  $Q$  the heat absorbed in the reaction



it follows from the definition of  $K$  that

$$d \log K/dT = -Q/RT^2.$$

Further writing

$$d \log k_{bi}/dT = E_{\text{reactants}}/RT^2,$$

where  $E_{\text{reactants}}$  is the sum of the critical increments of sucrose dihydrate and unhydrated hydrogen ion with respect to the inversion process, we have

$$E_{\text{reactants}} = 40,200 - Q.$$

It is evident that, to evaluate  $E_{\text{reactants}}$ , a knowledge of  $Q$  is required. This is not given by an examination of the inversion process itself. Moreover, since sucrose does not form a solid hydrate, its heat of hydration is not known. From an inspection, however, of the observed heats of hydration of other sugars,  $Q$  would appear to be about 5000 calories. Hence it follows that, for the process of inversion,  $E_{\text{reactants}}$  is equal to 35,000 calories, in round numbers. This quantity represents the sum of the individual critical increments of the sucrose dihydrate and unhydrated hydrogen ion. This, it will be observed, is decidedly greater than the critical increment calculated *directly* from the unimolecular velocity constants themselves.

*Sulphuric Acid as Catalyst.*

It is necessary to see whether the conclusions arrived at in the preceding section regarding the mechanism of inversion, based on the results obtained with hydrochloric acid as catalyst, are equally applicable to the case in which sulphuric acid is employed. For this purpose the data previously obtained by Jones and Lewis (*loc. cit.*) are given in the following table, the final column of which contains the values of  $k$  ( $=k_{bi}/K$ ) calculated in precisely the same manner as in tables V and VI.

TABLE VI.

N/10-Sulphuric acid as catalyst. Temperature = 20°.

Grams of sucrose per 100 c.c. of solution.	$k_{obs.} \times 10^6$	$k_i \times 10^6$	$a_H$	$a_{H_2O}$	$\eta$	$\eta^{0.52}$	$k \times 10^6 = \frac{k_{bi}}{K} \times 10^6 = \frac{k_{bi} \times a^2_{H_2O} \times \eta^{0.52} \times 10^6}{a_H}$
0	4.14	4.14	0.060	1.000	0.01035	0.0923	6.40
10	4.43	4.05	0.068	0.994	0.01359	0.1069	6.44
20	4.79	3.98	0.078	0.987	0.01857	0.1258	6.26
30	5.21	3.89	0.0895	0.979	0.02707	0.1531	6.38
40	5.54	3.68	0.105	0.968	0.04215	0.1884	6.33
50	5.95	3.455	0.118	0.955	0.07063	0.2520	6.73
60	6.22	3.09	0.139	0.938	0.1314	0.3481	6.81
70	6.29	2.58	0.162	0.914	0.2673	0.5135	6.69
Average $k_{30^\circ} = 6.51 \times 10^{-6}$ .							

Temperature = 40°.

Grams of sucrose per 100 c.c. of solution.	$k_{obs.} \times 10^6$	$k_i \times 10^6$	$a_H$	$a_{H_2O}$	$\eta$	$\eta^{0.52}$	$k \times 10^4 = \frac{k_{bi}}{K} \times 10^4 = \frac{k_{bi} \times a^2_{H_2O} \times \eta^{0.52} \times 10^4}{a_H}$
0	5.98	5.98	0.050	3.150	0.00659	0.0631	7.49
10	6.73	6.15	0.056	3.131	0.00846	0.0726	7.82
20	7.37	6.12	0.062	3.109	0.01138	0.0853	8.14
30	8.04	6.00	0.078	3.083	0.01593	0.1025	7.49
40	8.80	5.85	0.091	3.049	0.02364	0.1275	7.62
50	9.53	5.53	0.109	3.008	0.03731	0.1637	7.51
60	10.22	5.07	0.130	2.887	0.06530	0.2228	7.25
70	10.92	4.47	0.152	2.875	0.1260	0.3200	7.80
Average $k_{40^\circ} = 7.64 \times 10^{-4}$ .							

It will be observed that the values at both temperatures in the final column are reasonably constant. The mechanism assumed applies therefore in this case. Further, the energy term,  $E_b$ , calculated from the change of  $k$  ( $=k_{bi}/K$ ) with temperature, allowance being made as before for the substitution of saturated vapour in place of the vapour pressure in the case of water, leads to the

value 42,000 calories, which is in reasonably good agreement with the value 40,200 calories obtained with hydrochloric acid as catalyst. The lower value is regarded, however, as the more accurate.

*Alternative Mechanisms and Reasons for their Rejection.*

Inversion mechanisms other than that employed above were considered and rejected either on the ground of requiring unsatisfactory values of  $x$  or of leading to too great values for the critical increment. Of these the only one which appears to possess any likelihood is that involving unhydrated sucrose and hydrated hydrogen ion. It is found that a satisfactory constant for  $k_{bi}$  is obtained if the value ascribed to the power of the viscosity is  $x = 0.54$  at  $25^\circ$  and  $x = 0.58$  at  $35^\circ$ . These values in themselves are in accord with conductivity data. On this basis, however, the sum of the critical increments of unhydrated sucrose and hydrated hydrogen ion is found to be 49,000 calories, which seems excessive. On statistical grounds, the probability of complete dehydration of a sucrose molecule is small compared with that for partial dehydration such as is required by the process already considered in detail, and consequently this alternative process is regarded as less likely than the one given in the preceding section.

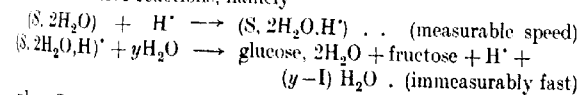
SUMMARY.

1. Electrometric measurements of the activity of hydrogen ion in various aqueous mixtures of sucrose and hydrochloric acid have been made at  $25^\circ$  and  $35^\circ$ .

2. From an analysis of the osmotic and vapour pressure determinations of aqueous solutions of sucrose, the activities of sucrose and water have been calculated.

3. Values for the true unimolecular velocity constants of inversion in terms of activity have been calculated from the observed velocity constants.

4. Using the data referred to above, the mechanism of the inversion process has been examined. It appears to involve the viscosity of the solution and it is shown that the power 0.52 to which the viscosity has to be raised to account for the velocity effect at  $25^\circ$  is practically that required to account for the conductivity behaviour. Stoichiometrically, the process of inversion involves two consecutive reactions, namely



where  $S$  stands for an unhydrated sucrose molecule.

5. The sum of the critical increments of sucrose dihydrate and unhydrated hydrogen ion is calculated to be approximately 35,000 calories.

One of the authors (T. M.) desires to express his indebtedness to the Department of Scientific and Industrial Research for the award of a grant.

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CXCIV.—*Studies on Hypophosphorous Acid. Part IV.*  
*Its Reaction with Cupric Chloride.*

By ALEC DUNCAN MITCHELL.

It has been shown in previous communications (T., 1920, 117, 1322; 1921, 119, 1266) that hypophosphorous acid effects reduction by means of an "active" form, which is designated, for purposes of formulation, as the fully hydroxylated compound  $\text{H}_2\text{PO}_3$ , but the precise constitution will, it is hoped, be elucidated by some projected experiments with alkyl derivatives—the dialkylphosphinic and alkylphosphinous acids. The active form reduces iodine and mercuric chloride rapidly, and the velocity of reduction is independent of the concentration of iodine or mercuric chloride (unless it is very dilute) and is conditioned solely by the rate of formation of the active form from hypophosphorous acid *molecules*. It follows that the *molecules* are normally in equilibrium with a small proportion (probably much less than 1 per cent.) of this active form. Baly has suggested (*Ann. Reports*, 1921, 18, 41) that this time-reaction is due to the activation of the *molecules* by the catalyst, which is giving to them the required energy increment, but this is a physical generalisation which doubtless constitutes a stage in all reactions, and in this case a purely chemical explanation for the time-reaction is quite possible. The oxy-acids of phosphorus exhibit a marked tendency to assume the quinquivalent form, as is shown by the monobasicity of hypophosphorous acid and the dibasicity of phosphorous acid, and Arbuzov (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 687) has shown that the trialkyl oxygen-esters of phosphorous acid readily pass into the quinquivalent form,  $\text{P}(\text{OR})_3 \longrightarrow \text{PRO}(\text{OR})_2$ , so that the possible existence of the tervalent form of hypophosphorous acid,  $\text{HP}(\text{OH})_2$ , which would be very reactive, supplies a chemical explanation.

The reaction between hypophosphorous acid and copper sulphate is interesting in that the salt is reduced ultimately to the hydride,  $\text{Cu}_2\text{H}_2$ . The products of this reaction in weakly acidic solution have been studied by Firth and Myers (T., 1911, 99, 1329), who showed that one obtained a mixture of hydride, phosphate, and suboxide, and it appeared to be of interest to follow the course of the reaction kinetically. A few preliminary experiments showed, however, that it was even more complicated than anticipated, and, in the hope of elucidating the earlier stages of the reaction, cupric chloride was studied instead, since, in the dilutions used, this is reduced only to cuprous chloride, and the hypophosphorous acid is oxidised only to phosphorous acid. It is found that, in this case also, the velocity of reduction is independent of the concentration of the copper if it exceeds decimolar, and is almost identical with the rates of reduction of iodine and mercuric chloride in similar circumstances, being limited by the rate of change of hypophosphorous acid to its active form.

The chief interest centred, therefore, in the examination of the reaction in very dilute solutions of copper chloride, where this reaction becomes so slow that it is of a lower order than that of the change  $\text{H}_3\text{PO}_2 \longrightarrow \text{H}_3\text{PO}_3$ , and is then the only measurable reaction. The change is represented stoichiometrically by the equation:  $\text{H}_3\text{PO}_2 + 2\text{CuCl}_2 = \text{H}_3\text{PO}_3 + \text{Cu}_2\text{Cl}_2 + 2\text{HCl}$ , but mathematical analysis shows that this reaction also is composed of two stages. The results are necessarily very complex, and their interpretation rests, to some extent, on circumstantial evidence, since their complete mathematical treatment (although fairly confirmatory so far as it goes) is limited by lack of data as to the two-stage ionisation of cupric chloride. It is hoped, however, that the results will prove of use in the further study of the reaction with copper sulphate, which is relatively so slow that it is independent of the hypophosphorous acid change, and depends only on the reaction between "active" acid and copper sulphate.

The discussion can be divided into three parts:

(a) Comparatively strong copper chloride solutions in which the slowest reaction is that concerning the change of hypophosphorous acid to its active form, and in which this constitutes the measurable reaction;

(b) Weak copper chloride solutions, in which the foregoing reaction is relatively so fast as not to affect the measured velocity, which concerns only the subsequent changes; and

(c) Solutions intermediate in strength between these two classes, in which the reactions are of the same order and are superimposed.

Case (a)—For copper solutions of this class, the method of treat-

ment adopted in previous communications (*loc. cit.*) is applied, with a slight modification due to the effect of the copper chloride on the ionisation of the hydrochloric acid. The "total ion" hypothesis, of which use has previously been made, assumes that, in a mixture of two binary electrolytes having a common ion, each has the same degree of ionisation that it would have if present alone in the same total ion concentration. This has not been extended to ternary electrolytes with any certainty, but is here adapted to the case of copper chloride as follows: the hypothesis is obviously equivalent to stating that the degree of ionisation for each electrolyte is the same as it would have been if present alone with the same concentration of the common ion, and in this form it is applied to the case under discussion. This modification is equally probable on theoretical grounds, in view of the theories of isohydric solutions, and is simpler in its application; moreover as the effect of the copper chloride in depressing the ionisation of the hydrochloric acid, as found by graphical means on this hypothesis, rarely exceeds 7 per cent., it is unlikely to cause an actual error of more than 1 per cent., but the error in the case of copper chloride itself may be much greater—a point which is discussed more fully later.

As before, for the reaction  $\text{H}_3\text{PO}_2 \longrightarrow \text{H}_3\text{PO}_3$  catalysed by hydrogen ions, one deduces the equation

$$ds/dt = kh_t l_t (1 - \alpha_t) \quad (1)$$

since the "active" acid is being utilised as fast as it is formed and the reaction is therefore direct and not reversible;  $l$  is the initial concentration of hypophosphorous acid and  $\alpha$  its degree of ionisation, whence  $l(1 - \alpha)$  is the concentration of the undissociated molecules;  $h$  is the total hydrogen-ion concentration initially, and  $k$  is the velocity coefficient for the direct equilibrium change ( $k_1$ , that for the reverse change, not being concerned in these cases). After a time  $t$ ,  $s$  is the concentration of phosphorous acid formed or of hypophosphorous acid oxidised; and the foregoing symbols have suffix  $t$  added:  $h$ , however, is nearly a linear function of  $s$ , and may be replaced by  $(h + ms)$ ,  $m$  being the mean coefficient of increase of  $h$  with  $s$  in any particular experiment;  $(1 - \alpha_H)$  is the value of  $(1 - \alpha)$  half-way through each particular period. The integration of (1) gives:

$$\begin{aligned} (1 - \alpha_H)(h + ml)kt &= \log_e(h + ms)/h + \log_e l/(l - s) \\ &= \log_e h_t/h + \log_e l_t/l \end{aligned} \quad (2)$$

The values of  $k$  in case (a) are moderately concordant and the mean ( $111 \times 10^{-5}$ ) is in fair agreement with those obtained in the cases of iodine and mercuric chloride,  $128 \times 10^{-5}$  and  $134 \times 10^{-5}$ .

respectively, there being a variety of causes which makes the lower value less accurate. Experiment 25 is shown in detail and the remainder are summarised in Table I.

## Experiment 25.

$$a = 99.7, m = 1.438, a_{\text{CuCl}_2} = 0.517, a_{\text{HCl}} = 0.850.$$

<i>t.</i>	2 <i>s.</i>	1 <i>s.</i>	$H^*_{\text{HCl}}$	<i>a.</i>	$1 - a_{\text{H}}$	$H^*_{\text{P}}$	<i>h.</i>	$k \times 10^5$ .
0	—	21.06	—	0.553	—	12.10	12.10	—
10	2.88	19.02	2.45	0.527	0.460	11.53	13.98	109
20	5.84	18.14	4.97	0.500	0.473	10.95	15.92	106
30	9.04	16.54	7.69	0.478	0.487	10.46	18.15	105
45	14.16	13.92	12.04	0.447	0.505	9.79	21.83	106
60	19.96	11.08	16.97	0.417	0.522	9.13	26.10	106
75	25.32	8.40	21.52	0.391	0.538	8.56	30.08	107
90	30.52	5.80	25.94	0.370	0.553	8.10	34.04	110
Mean								$107 \times 10^{-5}$

TABLE I.

Expt.	<i>a.</i>	<i>l.</i>	<i>a.</i>	$H^*_{\text{P}} = h.$	$k \times 10^5$ .	$a_{\text{HCl}}$	$a_{\text{CuCl}_2}$ .
*26	19.76	21.96	0.544	12.22	104	0.913	0.700
30	39.72	20.60	0.553	11.83	111	0.885	0.637
33	79.76	21.06	0.549	11.83	107	0.859	0.551
33a	78.56	21.96	0.544	12.22	113	0.859	0.551
36	30.00	20.60	0.553	11.83	110	0.895	0.668
37	49.84	20.60	0.553	11.83	111	0.878	0.616
Mean					$109 \times 10^{-5}$		

## Experiment 65.

$$a = 10.10, m = 1.418, a_{\text{CuCl}_2} = 0.553, a_{\text{HCl}} = 0.860, a_{\text{NaCl}} = 0.730.$$

<i>t.</i>	2 <i>s.</i>	1 <i>s.</i>	$H^*_{\text{HCl}}$	<i>a.</i>	$1 - a_{\text{H}}$	$H^*_{\text{P}}$	<i>h.</i>	$k \times 10^5$ .
0	—	10.58	—	0.650	—	7.02	7.02	—
5	0.27	10.44	0.23	0.646	0.352	6.98	7.21	104
10	0.58	10.29	0.50	0.640	0.354	6.91	7.41	106
20	1.18	9.99	1.03	0.630	0.360	6.80	7.83	106
30	1.83	9.66	1.57	0.618	0.365	6.68	8.25	105
45	2.88	9.14	2.48	0.602	0.372	6.50	8.98	107
60	4.05	8.55	3.48	0.586	0.382	6.33	9.81	109
75	5.27	7.95	4.54	0.571	0.390	6.17	10.71	110
90	6.54	7.31	5.62	0.556	0.398	6.00	11.62	111
105	7.58	6.79	6.52	0.544	0.406	5.87	12.39	108
Mean								$107 \times 10^{-5}$

TABLE II.

Expt.	<i>a.</i>	<i>l.</i>	<i>a.</i>	$H^*_{\text{P}} = h.$	$k \times 10^5$ .	$a_{\text{HCl}}$	$a_{\text{CuCl}_2}$	$a_{\text{NaCl}}$
63	10.00	20.49	0.551	11.83	117	0.860	0.553	0.730
66	19.92	20.94	0.551	11.83	126	0.855	0.532	0.730
69	20.13	10.58	0.650	7.02	114	0.855	0.532	0.730
Mean (including No. 65)					$116 \times 10^{-5}$			

Certain experiments carried out in the presence of *N*/2-sodium chloride gave similar constants which remained unaffected until the copper chloride became as dilute as *M*/50, although without

\* Only the initial value is recorded here as *a* is below *M*/10 (p. 1628).



additional sodium chloride the constancy began to fail when the copper became weaker than  $M/10$ . Experiment 65 is given as an example of the sodium chloride series, and the remainder are summarised in Table II.

As before, all concentrations are multiplied by 200 in order to avoid small decimals, and represent, therefore, gram-molecules per 200 litres. The initial molecular concentration of cupric chloride is denoted by  $a$ , wherefore  $(a - 2s)$  shows the concentration of unchanged cupric chloride.

The degrees of ionisation of the three chlorides are indicated by  $\alpha$  with the appropriate suffix, these being a mean in each experiment, the values at the beginning being slightly less, and those at the end slightly greater. The method whereby these are obtained is described later, but the increasing proportion of the highly ionised hydrochloric acid nearly compensates for the loss of chloride ions as cuprous chloride, and thus nearly maintains constancy of these values in each experiment.

$H_{HCl}$  represents the hydrogen-ion concentration derived from the hydrochloric acid, and  $H_P$  that derived from the hypophosphorous and phosphorous acids, which have nearly the same degree of ionisation, and which have a constant molecular total, allowance being made for a small proportion of phosphorous acid originally present in the hypophosphorous acid.

The temperature was 25° throughout.

Case (b).—When the reaction is so slow that it proceeds at less than one-tenth of the rate at which the hypophosphorous acid is capable of being transformed into its active form under the particular conditions, the concentration of the active form may be regarded as constant and proportional to  $l' = l(1 - \alpha)$ , the concentration of the hypophosphorous acid molecules, for the active form is produced at the rate  $kh'l' = k_1hy$ ,  $y$  being its concentration at any particular moment, and it is being used at the rate  $ds/dt$ ;  $y$  will be slightly less (say, by  $\delta y$ ) than its true equilibrium value, which is  $y_e = kh'l'/k_1h$ , so that  $dy/dt = kh'l' - k_1h(y_e - \delta y) = ds/dt$ , and as  $dy/dt$  is small compared with  $ds/dt$  and still smaller compared with  $kh'l'$ , one may put

$$(y_e - \delta y) = (kh'l' - ds/dt)/k_1h = kl'z/k_1(z + 1),$$

where  $z = kh'l'/(ds/dt) - 1$ ; that is,  $y = (y_e - \delta y) \propto l'(z/z + 1)$ , and in the case under discussion we are considering only velocities such that  $ds/dt$  is less than  $kh'l'/10$ , that is,  $z > 9$ , that is, if  $y$  is taken as proportional to  $l'$  the error involved will be 10 per cent. when the velocity is one-tenth of the maximum, or 2 per cent. when it is one-fiftieth of the maximum, and so on.

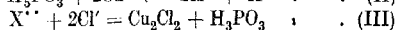
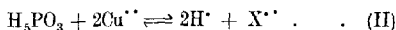
From a consideration of the velocities obtained when  $z$  is greater than 9, it was found that (1) when all other concentrations were constant, or nearly so, the velocity was very nearly proportional to  $l'$ , the concentration of the hypophosphorous acid molecules; and (2), similarly, other concentrations being constant, the velocity was very nearly proportional to the square of the concentration of the cupric chloride. The experiments carried out with the addition of sodium chloride, intended to depress the ionisation of the copper chloride, showed an increase in velocity which was much greater than could be attributed to the increase in the un-ionised copper chloride molecules, and which therefore directed attention to the part played by the chloride ions. In addition to this, the substitution of  $N/10$ -hydrochloric acid for  $N/10$ -sodium chloride unexpectedly gave much lower velocities, in spite of the fact that the un-ionised hypophosphorous acid molecules were increased, and pointed to a retarding effect of the hydrogen ions on the secondary reactions.

Owing to the complex action of each ion on several others, Ostwald's method of isolation could not be profitably employed, but for each small range of  $c$ , the chloride ion concentration (over which the ionisation of the copper chloride was nearly constant) the expression  $(ds/dt)h^2/l'a^2c^2$  gave fairly concordant results (except in certain cases) and, in any particular experiment, gave a constancy which was well within the limits of experimental error of  $ds/dt$ . On the other hand, expressions such as  $(ds/dt)/la^2$  and  $(ds/dt)/l'a^2c^2$  showed wide divergences (from  $0.7 \times 10^{-5}$  to  $525 \times 10^{-5}$ , and from  $0.5 \times 10^{-7}$  to  $60 \times 10^{-7}$  respectively) and fell off slowly but regularly in each experiment.

The retarding effect of hydrogen ions on the secondary reaction is also found in experiments with copper sulphate, where the primary change of hypophosphorous acid is relatively so rapid as not to be noticeable. It also explains a result which at first appeared anomalous, namely, that in approximately  $M/80$ -solutions of cupric chloride, with no additional hydrochloric acid or sodium chloride,  $M/10$ -hypophosphorous acid effected reduction somewhat less rapidly than  $M/20$ -acid, which is now seen to be due to the fact that the increase in the hypophosphorous acid is more than counterbalanced by the increase in the square of the hydrogen-ion concentration.

It therefore appears probable that, in the case of the copper chloride, an intermediate compound is formed by an equilibrium which is depressed by hydrogen ions, and that this compound reacts with chloride ions to give the final products of the reaction.

Omitting the stage concerning the formation of the active acid, these reactions could be formulated:



where  $\text{X}^{**}$  is the intermediate complex, the active part of the copper being assumed to be the metallic ion, since it is difficult to understand the part played by the chloride ions if the cupric chloride molecule takes part. The equilibrium in which the hydrogen ion plays a part can only be an intermediate stage, since the other end-products of the stoichiometric reaction  $\text{H}_3\text{PO}_3 + 2\text{CuCl}_2 = \text{H}_3\text{PO}_3 + \text{Cu}_2\text{Cl}_2 + 2\text{HCl}$ , do not appreciably affect the velocity of reaction when added in excess initially, corrections being made, of course, for the effect of the phosphorous acid on the hydrogen ion and hypophosphorous acid molecule concentrations, and the last stage is therefore not reversible. Moreover, the results obtained in the presence of  $N/2$ -sodium chloride for the change of hypophosphorous acid to its active form—case (a)—show that the active mass of the hypophosphorous acid is not affected by the sodium chloride, and the effect on the hydrogen ions is approximately equal to the small depression calculated. These results also show that the sodium chloride cannot affect these reactants appreciably by any virtual concentration due to hydration of the sodium or chloride ion, and therefore it cannot have any similar mechanical effect on the other reactant, copper chloride.

Additional support is given to the hypothesis under discussion by the fact that there is a marked lag in the first few minutes of an experiment when  $h$  is large compared with  $c$ , or vice versa, which would tend to make either of the reactions (II) or (III) much slower than the other.

Developing this hypothesis mathematically, if  $x$  is the concentration of the intermediate compound, we have for the formation and decomposition of  $y$  (the active acid):

$$dy/dt = (kh' - k_1hy) - (dx/dt + ds/dt) \quad . \quad . \quad . \quad (3)$$

for the formation and decomposition of the complex:

$$dx/dt = k_2(a - 2x)^2y - k_3h^2x - ds/dt \quad . \quad . \quad . \quad (4)$$

and for the final stage:

$$ds/dt = k_4xc^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$k_2$ ,  $k_3$ , and  $k_4$  being velocity coefficients.

At this point a slight difference of treatment is necessary according as the complex is assumed to react as a cuprous or a cupric compound, but both assumptions lead to results of the same type. Both  $x$  and  $y$  are very small and each is being used at almost the same rate as it is being formed, so that  $dx/dt$  and  $dy/dt$  may be

neglected in comparison with the other magnitudes in the equations in which they occur. Elimination of  $x$  and  $y$  from these three equations gives

$$(ds/dt) (1 + k_1h/k_2a^2 + k_1k_3h^3/k_2k_4c^2a^2 + 4khl'/k_4c^2a) = kh'l' \quad (6)$$

the last term in the parentheses occurring only if the complex is assumed to be cupric, and the second power of  $ds/dt$  being neglected. Now we are considering, for the present, only cases in which  $kh'l'/(ds/dt)$  is greater than 10, so that the unit in the parentheses may be neglected as an approximation, and one has

$$(ds/dt) (rh^2/l'a^2c^2 + r_1/l'a^2 + r_2/ac^2) = k \quad (7)$$

where  $r$ ,  $r_1$ , and  $r_2$  replace the other constants. The integration of this equation is cumbersome and calculations are therefore based only on the differentials, a method which makes them much more sensitive to experimental error, but much more capable of detecting changes in the course of the reaction which may be overlooked in the smoothing process of integration.

Various modifying assumptions give rise to similar expressions, but always the terms in the brackets decrease with decreasing values of  $a$  except the term  $(ds/dt) h^2/l'a^2c^2$ , which is very nearly constant, allowing for the rise in the value of  $z$  during the course of an experiment. If  $r_1$  and  $r_2$  are very small compared with  $r$ , which would be the case if the equilibrium (II) is rapidly attained and is only slightly displaced towards the right, one has

$$(ds/dt)h^2/l'a^2c^2 = K \quad (8)$$

where  $K = k/r$ .

An alternative hypothesis, assuming ionisation of the active acid to give two hydrogen ions and a bivalent anion which reacts, would require a similar mathematical expression, but receives no support from the iodine series, in which the active mass of the active form was apparently unaffected by hydrogen ions. The same expression would result from the assumption that the latter part of the reaction was really quinquemolecular between one molecule of active acid, two cupric ions, and two chloride ions, and that hydrogen ions acted anticatalytically corresponding with the square of their concentration; this assumption, however, has no precedent as regards the function of the hydrogen ions, and is therefore rejected in favour of the hypothesis developed above.

In Table III are shown, for a number of experiments, the range of values of  $a$  for which the condition applies that  $z$  is greater than 10, this range covering sometimes the whole experiment and sometimes only the last stages of an experiment; the mean values of  $l'/c$ , and  $h$ , over the range used, the extreme values being usually about one unit on either side in the case of  $h$ , and less than half a

unit in the cases of  $c$  and  $l'$ ; the degree of ionisation of the cupric chloride; and the mean value of the expression  $(ds/dt)h^2/l'a^2c^2 = K$ , from which is derived the value of  $r = k/K$ ,  $k$  being  $111 \times 10^{-5}$ , as obtained in case (a). The column headed "Remarks" refers to initial conditions in the experiments annotated. Experiment 42 is a detailed example, and is chosen, although the constancy is not so good as in the majority of cases, because it is one of the experiments in which both  $h$  and  $c$  are low and, as their relative changes are correspondingly high, they constitute a more crucial test of the accuracy of the expression than in cases in which  $h$  or  $c$  is raised by the addition of hydrochloric acid or sodium chloride; in this case the ratio  $h^2/c^2$  changes, in the course of the experiment, from 8.01 to 13.15. The slight rise in the value of  $K$  would be somewhat decreased if one took into account the fact that  $l'$  should be decreased by about 2 per cent. in the value for  $t = 40$  (see p. 1628), thus increasing  $K$  by that extent, and by only 0.5 per cent. in the value at  $t = 380$ . This correction has been ignored throughout the consideration of case (b), but it is automatically rectified in case (c) by the introduction of the term  $(ds/dt)/hl'$ .

## Experiment 42.

(l = 10.01—10.02 throughout).

$t$ .	2s.	a-2s.	l-s.	H <sub>2</sub> Cl.	a.p.	H <sub>2</sub> P.	h.	c.	$10^5 \times \frac{ds}{dt}$ .	$K \times 10^6$ .
0	—	2.466	21.96	—	0.544	12.22	12.22	4.32	—	—
40	0.171	2.295	21.87	0.16	0.542	12.18	12.34	4.20	385	316
80	0.310	2.156	21.80	0.30	0.540	12.13	12.43	4.10	318	315
120	0.426	2.040	21.75	0.41	0.539	12.11	12.52	4.01	268	314
160	0.526	1.940	21.70	0.50	0.538	12.09	12.59	3.93	233	324
220	0.654	1.812	21.63	0.63	0.537	12.07	12.70	3.84	193	322
270	0.745	1.721	21.59	0.71	0.536	12.05	12.76	3.76	168	326
320	0.825	1.641	21.55	0.79	0.535	12.03	12.82	3.70	147	328
380	0.904	1.562	21.51	0.87	0.534	12.01	12.88	3.65	129	330
454	0.994	1.472	21.46	0.95	0.533	11.98	12.93	3.57	—	—

Mean  $322 \times 10^{-6}$ 

When 2s = 0,  $a\text{CuCl}_2 = 0.872$ ,  $a\text{HCl} = \text{---}$ ,  
 2s = 0.5, 0.881, 0.960.  
 2s = 1.0, 0.888, 0.962.

It will be noticed that, as a rule, the value of  $K$  decreases at first more rapidly than the square of the apparent degree of ionisation of the cupric chloride, and then becomes almost independent of this function. If one applies the principles of the "total ion" hypothesis to each stage of the dissociation of cupric chloride, one finds that the first addition of extraneous chloride ions to dilute cupric chloride solutions produces a relatively large effect on the concentration of the cupric ion, most of its decrease being transferred to the undissociated molecule and very little to the  $\text{CuCl}'$  ion; as the concentration of the extraneous chloride ion increases, the

TABLE III.

Expt.	$\alpha$ .	$V$ .	$C$ .	$h$ .	$\kappa_{CuCl_2}$ .	$N \times 10^4$ .	$z$ .	Remarks.
42	2.5-1.4	10.0	4	12.5	0.88	322	3.4	
43	4.2	13.9	4	7.5	0.88	300	3.1	
91	2.5-2.1	12.9	4	27	0.88	350	3.2	App. N/10-HNO <sub>3</sub> added.
40	4.3-2.6	9.2	7	12.5	0.83	192	5.8	
45	2.7-2.0	3.6	7	9	0.83	221	5.0	
90	5.0-3.4	12.8	8	28	0.83	205	5.4	App. N/10-HNO <sub>3</sub> added.
29	4.3-2.9	9.7	12	16.5	0.79	145	7.7	
92	2.5-1.1	11.8	13.5	20.5	0.78	145	7.7	App. N/20-HCl added.
89	4.9-2.2	11.7	16	21	0.76	132	8.5	
41	2.5-1.3	13.0	22.5	28.5	0.73	143	7.8	App. N/10-HCl added.
43	2.5-1.1	6.2	22.5	25	0.73	138	7.0	
77	2.5-1.4	2.9	23	22.5	0.73	168	6.6	
34	2.5-2.5	6.0	25.5	26	0.71	148	7.5	
35	4.4-1.7	12.8	25.5	29.5	0.71	135	8.4	
76	4.5-2.0	2.7	25.5	23.5	0.71	157	7.0	
61	4.1-2.4	4.8	30	29.5	0.69	113	7.8	
62	4.2-2.2	11.8	29.5	33	0.69	126	8.8	
74	1.2-0.6	3.8	43	10	0.65	83	13.4	App. N/4-NaCl added.
85	0.7-0.4	4.0	41	8.5	0.65	84	13.2	
87	1.0-0.7	9.8	43	15	0.65	83	13.4	
88	1.4-0.6	10.0	41	13.5	0.65	80	13.0	
74	0.4-0.2	9.8	77	15	0.57	103	10.8	App. N/2-NaCl added.
70	0.7-0.3	10.0	75	13.5	0.57	98	10.2	
71	0.4-0.2	3.9	75	14.8	0.57	98	12.3	
78	2.1-1.0	9.7	22	14.5	0.73	93	11.2	App. N/10-NaCl added.
79	1.9-0.9	10.0	19.5	13.5	0.74	91	12.3	
81	1.3-0.8	3.9	19.5	18.5	0.74	102	10.9	
101	2.5-0.7	12.9	44	28.5	0.65	130	8.5	App. N/10-HCl and
102	2.5-0.7	6.1	45	28.5	0.65	132	7.8	N/20-NaCl added.
103	2.5-0.8	13.0	37.5	28.5	0.67	124	8.9	App. N/10-HCl and
104	2.5-0.9	3.6	38	24.5	0.67	138	8.0	N/10-NaCl added.
95	2.5-0.7	15.1	52	46	0.63	174	6.4	App. N/4-HCl added.
105	2.5-0.8	14.6	42.5	47	0.63	157	7.1	App. N/5-HCl added.

relative effect on the cupric ion becomes smaller and smaller, and this depression is transferred more and more to the  $\text{CuCl}'$  ion, and correspondingly less to the undissociated molecule. When one considers that, on the hypothesis developed analytically, the cupric ion is assumed to be the active part of the cupric chloride, and that to obtain comparable constants one should divide the values of  $(ds/dt)h^2/l'a^2c^2$  by  $\alpha^2_{\text{CuCl}_2}$ , it is at once seen that the tabulated values fall into line, qualitatively, with the requirements of the dissociation theory outlined in this paragraph. The substitution of hydrochloric acid by nitric acid gives results in good agreement with these ideas, but experiments in which more concentrated hydrochloric acid was used, or in which both sodium chloride and hydrochloric acid were used, give anomalous results, showing a tendency to rise with increasing concentrations of hydrochloric acid, but in each experiment  $K$  remains satisfactorily constant in spite of the change in the value of  $h^2/c^2$ . The experiments in which  $N/10$ -sodium chloride was used give results agreeing with those from  $N/4$ - and  $N/2$ -sodium chloride in spite of some difference in the degree of ionisation of the cupric chloride. Many attempts have been made to evolve an hypothesis which would bring these experiments into line, but in the absence of definite knowledge as to complex ions, of which the formation would be very slight in dilute chloride solutions but possibly appreciable in the presence of greater concentrations of chloride ions, the subject seems incapable of further discussion.

The objection may be urged that reaction (III) is an ionic one and therefore should be instantaneous, but there are several examples in the literature of ionic reactions occupying appreciable time, especially when they involve several ions and are not uni- or bimolecular, for example, that between bromic and hydrobromic acids (Judson and Walker, T., 1898, **73**, 410), which is bimolecular with regard to hydrogen ions and unimolecular with regard to both bromate and bromide ions.

Case (c).—Owing to the somewhat unsatisfactory nature of the results in case (b), it is superfluous to treat the experiments in this case in any detail. Here the unit in parentheses in equation (6) cannot be neglected, but, neglecting the terms which were found to be small in case (b), one has:

$$\begin{aligned} (ds/dt)(1 + rh^3/c^2a^2) &= kh', \\ \text{or } (ds/dt)/hl' + rK &= k \end{aligned} \quad (9)$$

where  $(ds/dt)h^2/l'a^2c^2 = K$ , as in (8), and  $r$  has the same significance as in (7).

For each experiment a value of  $r$  was selected which gave the

most constant value of  $k$ , and the mean values of  $k$  thus obtained in twenty-seven experiments ranged from  $102 \times 10^{-5}$  to  $114 \times 10^{-5}$  with a mean of  $109 \times 10^{-5}$ . The values of  $r$  thus utilised showed the same general characteristics as those in Table III.

#### EXPERIMENTAL.

The general method of procedure was similar to that used in the cases of iodine and mercuric chloride (*loc. cit.*).

An important modification was necessary, however, in order to avoid atmospheric oxidation of the cuprous chloride, which, in dilute solutions, often exceeded the rate of reduction of the cupric salt. For this purpose, the whole reaction was carried out in an atmosphere of carbon dioxide. The gas, generated in a Kipp's apparatus, was passed through two wash-bottles containing dilute cupric chloride solution and then, by means of a three-way tap, was directed either (a) through a tube reaching to the bottom of the liquid in the reaction-flask, from which it escaped by way of an outlet provided with rubber tubing and a screw-clip which regulated its flow, or (b) to the top of a 5 or 20 c.c. pipette fitted with a side-tube and a tap, similar in pattern to the 2 c.c. pipette recommended by Ostwald for the calibration of burettes. When a titration was required, the screw-clip on the reaction-flask was closed and a three-way tap in branch (b) leading to a mercury-trap was opened, so that some of the liquid was forced out of the flask by another tube connecting with the side-tube of the pipette until it reached slightly above the top mark of the pipette. Communication with the flask was now cut off by closing a screw-clip on the connecting tube, and the mercury-trap was cut out and branch (b) put into action so that, on opening the tap of the pipette, the liquid could be accurately adjusted to the top mark, and subsequently run off into the titration-flask until it reached the bottom mark. The liquid remaining in the pipette was forced back into the reaction-flask by opening the two screw-clips, and by re-opening branch (a) the cycle was completed.

The requisite amount of concentrated hypophosphorous acid (usually 2 or 4 c.c. of acid,  $d$  1.14) was placed in a small tube suspended inside the flask by means of a piece of thread passing through the outlet tube. At zero-time the tube could be upset and its contents rapidly mixed with the contents of the flask, which consisted of a definite volume (usually 100 or 200 c.c.) containing the cupric chloride and other reagents as required.

The nozzle of the pipette delivered the liquid below the surface of a solution containing excess of potassium iodide and sufficient sodium acetate to neutralise the "strong" acids, so that the



reaction was stopped completely before any cuprous chloride came into contact with the air, and the titration was carried out with sodium thiosulphate solution of appropriate strength. The whole operation, except the draining of the pipette and fine adjustment of the titration, occupied less than thirty seconds with practice, and could be timed so that the pipette was half-empty at any given time within one or two seconds.

Blank experiments in which solutions of cupric chloride of known thiosulphate titres were added to a mixture, such as would be obtained, of potassium iodide, sodium acetate, hydrochloric acid, hypophosphorous and phosphorous acids, showed that the titre was invariably correct. Also, in order to check experiments in which nitric acid was used, a test experiment was carried out which showed that, under the same conditions, nitric acid and cuprous chloride did not react appreciably. Similarly, in the dilutions used, hypophosphorous and nitric acids had no mutual action.

For the calculation of the degrees of dissociation of hydrochloric acid and sodium and cupric chlorides in these experiments, graphic methods were used and curves were constructed for each of the three chlorides separately showing the relation between degree of ionisation and concentration of chloride ions. By the method of trial, a total concentration of  $\text{Cl}^-$  ions ( $c$ ) was then found, such that if  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  were the corresponding degrees of ionisation of the three chlorides respectively and  $c_1$ ,  $c_2$ , and  $c_3$  their respective concentrations, then  $c = c_1\alpha_1 + c_2\alpha_2 + 2c_3\alpha_3$ .

The data used were those of Bray and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781) for hydrochloric acid and sodium chloride, and of Kohlrausch for cupric chloride: the last were not corrected for viscosity, and therefore are not very accurate in the more concentrated solutions, but as they are doubtless statistical values which cover also the first-stage dissociation, their significance is uncertain in the stronger solutions in any case. On the other hand, except in case (a), the copper solutions are dilute, so that when the chloride concentration is small the error involved is slight, and when the chloride concentration is large the error is greater but is relatively small. A similar remark applies to the effect of the solubility of cuprous chloride on the chloride-ion concentration: the cuprous chloride is precipitated almost from the beginning in the weaker chloride solutions and the actual error is small, whereas, in the stronger chloride solutions, its solubility is greater and the precipitation is delayed, but the relative effect is small.

A series of experiments was carried out in the presence of a

mixture of *N*-phosphoric acid and *N*-potassium dihydrogen phosphate to regulate the hydrogen-ion concentration. In the iodine series these experiments gave very concordant values for a constant in the more concentrated solutions, this constant being  $265 \times 10^{-4}$  for what was virtually a unimolecular reaction consisting of the change of hypophosphorous acid to its active form. In the present experiments, when *a* exceeded 30, constants of  $260 \times 10^{-4}$ ,  $274 \times 10^{-4}$ , and  $270 \times 10^{-4}$  were obtained; the velocity is therefore the same in both series. With stronger solutions of copper chloride, the production of hydrochloric acid soon becomes so large as to overcome the effect of the regulator, and the constant rises. With weaker solutions, when *a* is less than 5, the main reaction is so rapid as not to affect the measurable velocity, and the values of  $(ds/dt)/la^2$  fall off slowly as in the ordinary solutions—case (b)—but the ionic relations are so complicated that it is impossible to draw any definite conclusions.

The irreversibility of the complete reaction was demonstrated by using a mixture of cuprous chloride, suspended in *N*/10-hydrochloric acid and *N*/10-sodium chloride, and *N*/10-phosphorous acid; the very slight oxidation of the cuprous salt was no greater than that obtained in blank experiments which had been devised to detect accidental oxidation, and was of a lower order than the slowest reduction-velocity recorded. The fact that all the reactions came very nearly to a standstill when the total reduction was equivalent to the hypophosphorous acid initially present also pointed to the irreversibility of the reaction. The latter fact, in addition, supports the results of other tests, made independently, which showed that reaction between cupric salts and phosphorous acid is negligible compared with that of hypophosphorous acid.

In all the data given,  $ds/dt$  is obtained from a smoothed curve of the first differentials, but the recorded values of *2s* are not smoothed. This method, although sensitive to experimental error, constitutes a far more rigid criterion of the nature of the reaction than an integrated constant, which often gives a misleading appearance of accuracy. Nearly all the experiments have been checked by duplicates, and the agreement is usually very close in actual titres, although naturally the values of  $ds/dt$ , even when smoothed, vary to a larger extent, but are correct to within 2 or 3 per cent.

#### Summary.

- (1) The first stage in this, as in similar reductions which have been described, is the change of hypophosphorous acid *molecules* to the active form, provisionally formulated as  $H_5PO_3$ ; this change is catalysed by hydrogen ions.

(2) In dilute copper solutions two succeeding reactions are detected: (a) an equilibrium in which the copper ion and the active hypophosphorous acid give a complex ion ( $X''$ ) and hydrogen ions, which therefore repress the reaction:  $H_3PO_3 + 2Cu' = X'' + 2H'$ ; and (b) a direct reaction between the complex and chloride ions:  $X'' + 2Cl' = Cu_2Cl_2 + H_3PO_3$ .

(3) The foregoing statement is based primarily on circumstantial evidence, but a certain amount of mathematical support is also adduced.

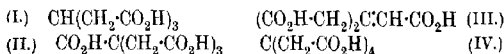
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CXCV.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part VII. iso-Butylene- $\alpha\gamma\gamma'$ -tricarboxylic Acid and Methanetetra-acetic Acid.*

By CHRISTOPHER KELK INGOLD and LEWIS CHARLES NICKOLLS.

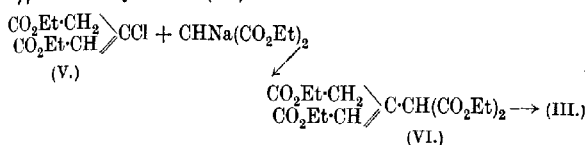
THE practical object with which this series of researches was instituted, namely, the preparation of the acids I, II, III, and IV, has now been accomplished. Methanetriacetic acid (I) (T., 1921, **119**, 352; this vol., p. 1419) and carboxymethanetriacetic acid (II) (T., 1921, **119**, 1871) have already been obtained in quantity, and methods for the preparation of *isobutylene- $\alpha\gamma\gamma'$ -tricarboxylic acid* (III) and *methanetetra-acetic acid* (IV) are now described.



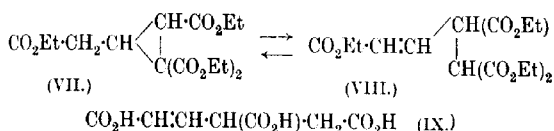
On the theoretical side, the experiments described in the present paper are a logical application of the general principles, previously elucidated (Parts I, II, III, IV, and VI), regarding the conditions of formation of branched-chain esters by the Michael condensation. Two main groups of phenomena influence these reactions: (a) the three-carbon tautomerism of the glutaric acids from which the polyacetic acids may be supposed, in an empirical sense, to be derived by the addition of one molecule of acetic acid (T., 1921, **119**, 341, 1222, 1865); (b) the reversibility of the Michael reaction (T., 1921, **119**, 1582, 1866; this vol., p. 1414), which has also been established for cases outside the methanetriacetic acid series (Ingold and Powell, T., 1921, **119**, 1976). The plan according to which the

new syntheses were devised was based on the knowledge that has been gained regarding the mode of operation of these two sets of conditions, and it may be in consequence of this that every one of the reactions proceeded according to expectation.

*iso*Butylene- $\alpha\gamma\gamma'$ -tricarboxylic acid was first synthesised in the following manner. Citric acid was converted successively into acetonedicarboxylic acid, ethyl acetonedicarboxylate, and  $\beta$ -chloroglutaconic acid by processes, improved in detail, but essentially similar to those described in the literature. The chloro-acid was then esterified, and the ester (V) condensed with ethyl sodiomalonate to give a product (VI), which, on hydrolysis, yielded *isobutylene*- $\alpha\gamma\gamma'$ -tricarboxylic acid (III):



This synthesis, although simple and convenient as a method of preparation, does not provide an adequate basis for the constitution assigned to the acid. The ester (V) is a mobile glutaconic ester, and therefore it is possible that the reaction consists in the 1:3-addition of ethyl sodiomalonate (compare Ingold and Thorpe, T., 1921, **119**, 492) followed by the internal elimination of sodium chloride. It is true that in this case the immediate product (VII) would not be unsaturated; but it *would* be the cyclic individual of a ring-chain three-carbon tautomeric system, and might pass partly or wholly into its open-chain unsaturated isomeride (VIII):

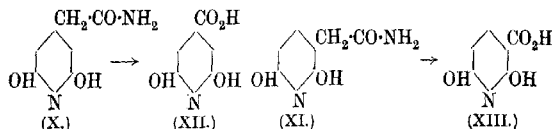


The ester actually obtained was unsaturated, and so also was the acid derived from it by hydrolysis; hence the decision lay between the formulæ (VI) and (VIII) for the ester, and between (III) and (IX) for the acid.

The first plan which was tried was based on the well-known method for converting mobile glutaconic acids into derivatives of 2:6-dihydropyridine by treating their esters with ammonia.

The pyridine derivative which could be obtained in this way from the unsaturated acid having formula (III) or (IX) would have formula (X) or (XI), and on cautious oxidation might give

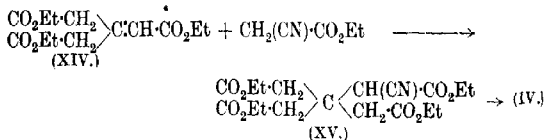
2:6-dihydroxyisonicotinic acid (XII) or 2:6-dihydroxynicotinic acid (XIII), both of which are known :



No difficulty was experienced in preparing a dihydroxypyridine-acetamide, which is now known to have formula (X) (not XI), but it could not be oxidised to a known acid because the mildest oxidising agents, even atmospheric oxygen, converted it into a bluish-green substance of comparatively large molecular weight. 2:6-Dihydroxypyridine itself also possesses this property, but to a much smaller extent.

The constitution of the unsaturated acid was ultimately settled by reduction. The acid was unaffected by sodium amalgam, aluminium amalgam, or the zinc-copper couple under ordinary conditions, whilst heating with hydriodic acid, with or without the addition of phosphorus, yielded gums. Finally, however, reduction was effected by means of sodium amalgam in boiling acid solution as described on p. 1645, and the product was identified as methane-triacetic acid (I), which conclusively establishes the formula (III) for the unsaturated acid. The tetracarboxylic ester must therefore have formula (VI), and not (VIII). *n*-Butane- $\alpha\beta\delta$ -tricarboxylic acid, the reduction product to be expected from an acid of the formula (IX), is known and has about the same melting point as methane-triacetic acid, but the identity of the reduction product actually obtained with methane-triacetic acid, and its non-identity with *n*-butane- $\alpha\beta\delta$ -tricarboxylic acid, was conclusively proved by direct comparison with synthetic specimens of each of these substances.

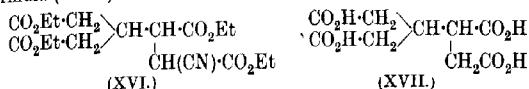
In order to obtain methane-tetra-acetic acid (IV), ethyl *iso*-butylene- $\alpha\gamma\gamma'$ -tricarboxylate (XIV) was condensed with ethyl cyanoacetate, the product (XV) yielding methane-tetra-acetic acid on hydrolysis :



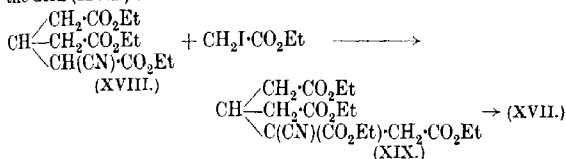
The yield of the condensation product (XV) amounted to 80 per cent. of the theoretical, whilst, as might be expected from what

has been written in the earlier parts of this series, ethyl malonate showed no tendency to condense with the unsaturated ester (XIV) under similar experimental conditions.

In considering this condensation, it is also necessary to take account of the possibility of 1 : 3-addition to the normal form of the glutaconic ester concerned. Such a reaction would lead to a cyano-ester having the formula (XVI), whilst the acid obtained on hydrolysis would not be methanetetra-acetic acid but an isomeric acid of formula (XVII) :



In order to settle the question, the acid (XVII) was synthesised by a method which left no doubt concerning its constitution. The starting point was ethyl  $\omega$ -cyanomethanetriacetate (XVIII), the structure of which rests, first, on its synthesis from ethyl  $\beta$ -hydroxyglutarate and ethyl cyanoacetate, and secondly on its hydrolysis to methanetriacetic acid (Ingold, T., 1921, **119**, 352). This ester was converted into its sodio-derivative and this condensed with ethyl iodoacetate to give a cyano-ester (XIX), which, on hydrolysis, yielded the acid (XVII) :



The acid was different from that obtained from *isobutylene*-dicarboxylic ester by condensation with ethyl cyanoacetate. The cyano-ester produced in this way must therefore have formula (XV) and not (XVI), whilst the acid obtained on hydrolysis must be methanetetra-acetic acid (IV).

The yields obtained in the reactions which lead from citric acid to methanetetra-acetic acid are good on the whole, and considerable amounts of this acid, and of *isobutylene*tricarboxylic acid, have already been prepared by the process described. The investigation of these acids is in progress.

From the crystallographic point of view methanetetra-acetic acid is of exceptional interest on account of its great symmetry. The systematic crystallographical examination of such symmetrical structures has been undertaken by Miss I. E. Knaggs of this College, whose results on methanetetra-acetic acid and certain related compounds will shortly be published.

## EXPERIMENTAL.

(A.) *Synthesis of isoButylene- $\alpha\gamma\gamma$ -tricarboxylic Acid from Citric Acid.*

*Acetonedicarboxylic Acid.*—The preparation of this substance from citric acid by Jerdan's method (T., 1899, 75, 809, footnote) is not always successful owing to the serious effect on the yield of very small variations in the experimental conditions. In the course of the present experiments the following process was thoroughly standardised. Two kilograms of fuming sulphuric acid ( $\text{SO}_3 = 15$  per cent.;  $d$  1.920) are added as rapidly as possible, with constant stirring, to one kilogram of finely powdered hydrated citric acid. A considerable amount of heat is evolved and large volumes of carbon monoxide escape. After fifteen minutes the mixture is cooled by a freezing-mixture (ice-salt), and one kilogram of crushed ice added with stirring. When cold, the pasty mass is filtered on glass-wool, and the solid pressed in a hydraulic press and then thoroughly dried on porous plates. The average yield is 450 grams, or about 80 per cent. of the theoretical.

*Ethyl Acetonedicarboxylate.*—The preparation of this substance has been described by Jerdan (*loc. cit.*), but, in our hands, his process gave very unsatisfactory results, to obviate which the following method was evolved as a result of many comparative experiments. Absolute ethyl alcohol (500 grams), saturated with hydrogen chloride at the ordinary temperature, is treated at  $0^\circ$  with 300 grams of dry acetonedicarboxylic acid. The suspension is shaken frequently to aid solution of the acid, and kept at the ordinary temperature for forty-eight hours, after which water is added and the ester isolated by extraction with ether. Ethyl acetonedicarboxylate and ethyl acetoacetate are easily separated by distillation under diminished pressure, and there is need to employ the tedious chemical separation used by previous workers. The quantity of ethyl acetoacetate in the crude ester is only 5–10 per cent., much less, therefore, than the amount contained in Jerdan's product. The yield of pure ethyl acetonedicarboxylate, b. p.  $141\text{--}143^\circ/15$  mm., is 240 grams, that is, 60 per cent. of the theoretical.

*$\beta$ -Chloroglutaconic Acid.*—Burton and von Pechmann's method (Ber., 1887, 20, 145) for preparing this substance consists in treating ethyl acetonedicarboxylate with phosphorus pentachloride (3 mols.) and hydrolysing the product. We were, however, unable to obtain by this means more than small traces of a very impure acid which seemed to be  $\beta$ -chloroglutaconic acid, but could neither be purified nor identified with certainty. The main product of the action of this proportion of phosphorus pentachloride on ethyl acetone-

dicarboxylate is a highly crystalline chloro-ester, m. p.  $96^{\circ}$ , not mentioned by Burton and von Pechmann, which does not appear to yield  $\beta$ -chloroglutaconic acid on hydrolysis. The chloro-ester is at present under investigation.

A satisfactory process for the preparation of  $\beta$ -chloroglutaconic acid was evolved from many comparative experiments. Ethyl acetonedicarboxylate (90 grams) and phosphorus pentachloride (95 grams) are mixed as rapidly as the brisk evolution of hydrogen chloride allows, the temperature being kept below  $50^{\circ}$ . When the reaction is finished, the mixture is poured into water, ice being added from time to time to prevent an undue rise of temperature as the phosphoryl chloride decomposes. The red oil is extracted with ether and hydrolysed by boiling for two and a half hours with 20 per cent. hydrochloric acid. The clear yellow solution is evaporated on a water-bath until it crystallises while still hot, and the acid dried in ethereal solution with calcium chloride. The acid thus obtained is free from gum and nearly pure, the yield being 51 grams, that is, 70 per cent. of the theoretical.

*Ethyl  $\beta$ -Chloroglutaconate* (V).—The above product (100 grams) was mixed with 300 grams of ethyl alcohol and 50 c.c. of sulphuric acid in a flask provided with a 10 cm. fractionating column attached to a condenser. The mixture was kept at its boiling point while alcohol vapour was passed in from another flask until 1.5 litres had collected in the receiver. The neutral ester was separated from a small trace of acid ester by adding water, extracting with ether, and washing with aqueous sodium carbonate. The yield of nearly pure ester, b. p.  $135\text{--}140^{\circ}/11\text{ mm.}$ , was 120 grams, that is, 90 per cent. of the theoretical.

*Ethyl  $\beta$ -chloroglutaconate* is a colourless, mobile oil with a characteristic sweet, fruity odour. It has b. p.  $136\text{--}137^{\circ}/11\text{ mm.}$  (Found: C = 48.9; H = 6.1; Cl = 16.1.  $\text{C}_9\text{H}_{13}\text{O}_4\text{Cl}$  requires C = 49.0; H = 6.0; Cl = 16.1 per cent.).

*Ethyl isoButylene- $\alpha\gamma\gamma'$ -tetracarboxylate* (VI).—Ethyl  $\beta$ -chloroglutaconate (1 mol.) was added to a cold suspension of ethyl sodium-malonate (1.2 mols.) in absolute ethyl alcohol. Sodium chloride rapidly separated with considerable evolution of heat, which caused the solvent to boil for a short time. The mixture was treated on the steam-bath for half an hour, then cooled, and poured into a large volume of water. The neutral oil, which was isolated by extraction with ether in the usual way, consisted of the tetracarboxylic ester with some unchanged ethyl malonate, which was easily removed by distillation. The *tetraethyl* ester boils at  $220\text{--}222^{\circ}/12\text{ mm.}$  with slight decomposition. The yield of the crude ester was about 65 per cent., and of the distilled ester 50 per cent., of the theoretical



(Found: C = 55.0; H = 6.8.  $C_{15}H_{24}O_8$  requires C = 55.8; H = 7.0 per cent.).

*Ethyl cyanoisobutylene-tricarboxylate*.—This substance, obtained by condensing ethyl  $\beta$ -chloroglutaconate with ethyl sodiocyanoacetate (2 mols.), boiled at about  $230^\circ/12$  mm., but it decomposed much more extensively than the preceding substance, and therefore could not be obtained pure for analysis.

*iso-Butylene- $\alpha\gamma\gamma$ -tricarboxylic Acid (III)*.—This acid was usually prepared by hydrolysing the tetra-ethyl ester with 20 per cent. hydrochloric acid. After boiling for forty-eight hours, the solution was evaporated on a water-bath. The syrupy acid obtained, the yield of which amounted to 85 per cent. of the theoretical, was pure enough for conversion into its ethyl ester (below); but on keeping for a few days it crystallised in clusters of needles, which, after recrystallisation from concentrated hydrochloric acid, from ether, or from a mixture of chloroform and acetone, melted at  $140^\circ$ .

Specimens of the syrupy acid which are too impure to solidify can easily be purified by conversion into the crystalline calcium salt and subsequent regeneration. The acid can thereafter be crystallised without difficulty.

The pure acid is very soluble in water, alcohol, or acetone, but only slightly soluble in ether, chloroform, or benzene (Found: C = 44.7; H = 4.4.  $M$ , by titration, = 188.2.  $C_7H_8O_6$  requires C = 44.7; H = 4.3 per cent.;  $M$  = 188). It instantly reduces cold alkaline permanganate.

*2:6-Dihydroxypyridine-4-acetamide (X) (The imide-amide of isobutylene-tricarboxylic acid)*.—This substance was prepared by the action of ammonia on ethyl isobutylene-tricarboxylate (below), but owing to the facility with which it was oxidised by oxygen to a blue-green compound of unknown constitution special precautions had to be taken to exclude air. The ester was placed in a sealed tube with twice its weight of aqueous ammonia previously saturated at  $0^\circ$ . The tube was furnished with a capillary neck at each end, the upper one containing a minute plug of asbestos. After keeping for one week at the ordinary temperature, when a mass of colourless needles had separated, the tube was placed in an inverted position within an inverted test-tube full of hydrogen, the capillaries were broken, and the crystals collected on the asbestos plug with the aid of a pump. They were washed with water and methyl alcohol and dried *in situ*, the whole operation being conducted in hydrogen. When dry, the crystals, m. p.  $228^\circ$ , are fairly stable, but they turn green at once on dissolving in water in the presence of air (Found: N = 16.85.  $C_7H_8O_3N_2$  requires N = 16.7 per cent.).

*Methanetriacetic Acid (I)*.—The general behaviour of isobutylene-

tricarboxylic acid towards reducing agents is described on p. 1640, and little need be added here excepting the details of the reduction to methanetriacetic acid. The acid (2 grams) was dissolved in 50 c.c. of water, and the solution kept boiling for four hours while 150 grams of 4 per cent. sodium amalgam were added, the liquid being maintained slightly acid by the occasional addition of hydrochloric acid. The aqueous solution was separated from the mercury, strongly acidified with hydrochloric acid, and evaporated to dryness. The methanetriacetic acid was extracted from the residue with ether, and after draining as completely as possible from the accompanying gum, was purified by crystallisation from ether, and identified by direct comparison and a mixed-melting-point determination with an authentic specimen.

The bromination products of *isobutylene*tricarboxylic acid are characteristic, and are at present being investigated.

*Ethyl isobutylene*tricarboxylate (XIV).—This ester was prepared by directly esterifying the acid with ethyl alcohol in the usual way. It is a colourless, mobile oil, b. p. 174–175°/11 mm. (Found: C = 57.1; H = 7.5.  $C_{13}H_{20}O_6$  requires C = 57.3; H = 7.3 per cent.). It shows no tendency to condense with ethyl sodiomalonate under the usual conditions of the Michael reaction, but it condenses easily with ethyl cyanoacetate (below.)

(B.) *Synthesis of Methanetetra-acetic Acid from isobutylene tricarboxylic Acid.*

It is not necessary to isolate pure ethyl *isobutylene*tetracarboxylate or pure *isobutylene*tricarboxylic acid in order to obtain the ethyl *isobutylene*tricarboxylate required for the preparation of methanetetra-acetic acid. The syrupy product of hydrolysis, obtained from the crude (undistilled) tetraethyl ester, was dried by dissolving in ether and shaking with calcium chloride, and then esterified with ethyl alcohol by the method described on p. 1643. The ester (b. p. 173–176°/11 mm.) was thus obtained in a yield of 80 per cent. of the theoretical calculated on the syrupy acid, or of 50 per cent. of the weight of ethyl  $\beta$ -chloroglutaconate employed.

*Ethyl  $\omega$ -Cyanomethanetetra-acetate* (XV).—The triethyl ester (13.6 grams) was added to a cold alcoholic suspension of ethyl sodiocyanoacetate prepared from 11.3 grams (2 mols.) of ethyl cyanoacetate, 2.3 grams of sodium, and 30 grams of ethyl alcohol. The mixture was heated for five hours on the steam-bath, and the gelatinous product mixed with excess of dilute hydrochloric acid and extracted with ether. The extract was washed with aqueous sodium carbonate and with water, dried, and evaporated, and the residue distilled. The *cyano-ester* (11 grams) boiled at 234–235°/13

mm., and was obtained as a viscous, pale yellow oil. The acid products recovered from the sodium carbonate washings yielded a further quantity on esterification with ethyl alcohol, the total yield amounting to 80 per cent. of the theoretical (Found: C = 56.0; H = 7.0; N = 3.88.  $C_{18}H_{27}O_8N$  requires C = 56.1; H = 7.0; N = 3.64 per cent.).

*Methanetetra-acetic Acid (IV).*—A mixture of the above cyano-ester with an equal volume of cold concentrated sulphuric acid was kept at the ordinary temperature for twelve hours, then diluted with two volumes of water and boiled for seven hours, care being taken to allow the alcohol vapour to escape freely from the condenser. The crystals which separated were filtered, and the filtrate evaporated until a further crop was obtained on cooling. Extraction of the strongly acid liquid with ether yielded a small additional quantity of crystalline material.

The crystals contained 2–3 per cent. of nitrogen, which was only slowly removed by boiling with 50 per cent. sulphuric acid or with 40 per cent. potassium hydroxide. Treatment with nitrous acid, however, rapidly eliminated the nitrogen and yielded methanetetra-acetic acid in the pure condition. The crystals were dissolved in forty times their weight of water, and treated with an excess of sodium nitrite and hydrochloric acid, the solution being slowly raised to the boiling point. When it had boiled for a few minutes, it was rendered exactly neutral by adding sodium hydroxide, and then treated with an excess of barium chloride. The copious flocculent precipitate became crystalline after keeping for twelve hours in contact with its mother-liquor, and was then collected, washed, and decomposed with hydrochloric acid. The acid solution was evaporated to dryness, and the powdered residue extracted with boiling acetone. The residue from the acetone was washed with ether and finally purified by crystallisation from water, from which the tetra-acetic acid separated in stout, well-formed, glistening octahedra. At 226° the acid begins to soften and a gradual loss of water takes place; when the temperature of the bath is raised rapidly, the acid melts at 248°, but sinters perceptibly below that temperature (Found: C = 43.3; H = 4.8.  $C_9H_{12}O_8$  requires C = 43.5; H = 4.8 per cent.). The acid is slightly soluble in ether, but is more soluble in acetone or water.

The barium salt of methanetetra-acetic acid is very insoluble and similar in many ways to the barium salt of the lower homologue, carboxymethanetriacetic acid, recently described (Ingold and Powell, T., 1921, 119, 1872). It may be obtained from extremely dilute solution in long, felted needles (Found: Ba = 52.6.  $C_9H_8O_8Ba_2$  requires Ba = 52.9 per cent.).

The silver salt is also unusually insoluble. It is obtained as a curdy precipitate, and is stable towards light (Found : Ag = 63·3,  $C_9H_8O_8Ag_4$  requires Ag = 63·9 per cent.).

The dianhydride,  $O \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown CO \cdot CH_2 \end{smallmatrix} C \begin{smallmatrix} \diagdown CH_2 \cdot CO \\ \diagup CH_2 \cdot CO \end{smallmatrix} O$ .—This substance is best prepared by heating the acid with acetyl chloride in a sealed tube at 140° for six hours. The anhydride, which, on cooling, crystallises in hexagonal plates, may be purified by crystallisation from acetone containing a trace of chloroform. It melts at 284°, and therefore resembles the dianhydride of carboxymethanetriacetic acid (Ingold and Powell, *loc. cit.*) in the unusual property of melting at a higher temperature than the corresponding acid (Found : C = 5·06; H = 3·6.  $C_9H_8O_8$  requires C = 50·9; H = 3·8 per cent.).

(C.) *Synthesis of isoPentane- $\alpha\beta\delta\delta'$ -tetracarboxylic Acid from  $\beta$ -Hydroxyglutaric Acid.*

The  $\beta$ -hydroxyglutaric acid (obtained from acetonedicarboxylic acid by reduction) was esterified, and then condensed with ethyl sodiocyanoacetate in the manner previously described (Ingold, *loc. cit.*), the product being ethyl  $\omega$ -cyanomethanetriacetate (XVIII). The sodio-derivative of this was then allowed to react with ethyl iodoacetate to give the following compound.

Ethyl  $\beta$ -cyanoisopentane- $\alpha\beta\delta\delta'$ -tetracarboxylate (XIX).—Ethyl  $\omega$ -cyanomethanetriacetate (10 grams) was added to a solution of sodium ethoxide prepared by dissolving 0·8 gram of sodium in 12 grams of absolute ethyl alcohol. This solution was mixed with 7·1 grams of ethyl iodoacetate and heated on the steam-bath for three hours, after which the product was cooled, poured into water, and extracted with ether. On distilling the residue from the extract, 9 grams of a colourless, somewhat viscous oil, b. p. 222–224°/10 mm., were obtained (Found : C = 56·1; H = 6·8.  $C_{18}H_{27}O_8N$  requires C = 56·1; H = 7·0 per cent.).

isoPentane- $\alpha\beta\delta\delta'$ -tetracarboxylic Acid. (XVII).—The cyano-ester was left in contact with an equal bulk of concentrated sulphuric acid for twenty-four hours, after which two volumes of water were added and the whole was boiled for seven hours. The products extracted by ether were syrupy, and therefore were heated for a further five hours with 20 per cent. hydrochloric acid to complete the hydrolysis, care being taken to allow alcohol vapour free escape. The residue obtained on evaporation soon solidified, and was then purified by crystallisation from a mixture of acetone and chloroform. The acid separated in needles, which melted at 182° (Found :

C = 43.1; H = 4.8.  $C_9H_{12}O_3$  requires C = 43.5; H = 4.8 per cent.). The acid is exceedingly soluble in water or acetone, but is sparingly soluble in chloroform or benzene.

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### CXCVI.—The Alkylhydrazones.

By OSCAR LISLE BRADY and GERALD PATRICK MCHUGH.

A CONSIDERABLE number of hydrazones have been found to exist in two forms. Lists of such compounds are given by Werner ("Lehrbuch der Stereochemie," 1904, 267), by Lockemann and Liesche (*Annalen*, 1905, **342**, 14), and by Vecchiotti (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 75). In addition, Forster and Zimmerlie (T. 1910, **97**, 2156; 1911, **99**, 478) have obtained isomeric hydrazones, semicarbazones, and phenylhydrazones of camphorquinone. In a number of cases the existence of the two forms is accounted for on the Hantzsch-Werner stereochemical theory, while in others it has been suggested that it is due to physical isomerism. The work of Lockemann and Lucius (*Ber.*, 1913, **46**, 150, 1013) has, however, shown that in two cases the supposed stereoisomerism does not exist, namely, the phenylhydrazones of benzaldehyde and salicylaldehyde.

The isolation of a second form has, so far, been due more or less to chance and no general method has appeared as in the case of the aromatic aldoximes. It seemed of interest to ascertain if the simpler hydrazones could be converted into isomerides through their hydrochlorides as in the case of the oximes. The hydrazones themselves are immediately converted by acids into the azines, so attention was directed to the alkylhydrazones. These compounds were chosen as more likely to form stable hydrochlorides than those derived from the arylhydrazines, an expectation which results have justified. The only compound of this type which has been described is benzaldehydemethylhydrazone,  $C_6H_5CH=N \cdot NH \cdot CH_3$  (Harries and Haga, *Ber.*, 1898, **31**, 62), obtained by the action of excess of methylhydrazine on benzaldehyde. As some difficulty arises in connexion with these compounds owing to the tendency of two molecules of methylhydrazine

to react with three molecules of the aldehyde to give compounds of the type  $\text{CHR}(\text{NMe}\cdot\text{N}(\text{CHR})_2)_3$ , the dimethyl- and diethylhydrazones have also been investigated. In the latter case only uncrystallisable oils were obtained even from aldehydes of high melting point. These oils, however, gave solid hydrochlorides and platinichlorides, but the decomposition of the hydrochlorides with sodium carbonate solution regenerated the hydrazone as an oil. If these compounds were mixtures of stereoisomerides, as might be expected from the difficulty in obtaining them solid, the conversion into hydrochloride and subsequent decomposition does not apparently convert them into one form. The dimethylhydrazone and methylhydrazone of *p*-nitrobenzaldehyde were obtained crystalline, but conversion into the hydrochloride and decomposition with sodium carbonate regenerated the original compounds.

Unfortunately this work has had to be abandoned for the time being owing to the toxic nature of the alkylhydrazines, but, as far as the limited number of compounds investigated show, there is no indication that the hydrochloride method will give rise to stereoisomerides. Experience in the case of the oximes, however, necessitates caution in rejecting the method without the study of a larger number of compounds, as many aromatic aldoximes cannot be converted into their isomerides through the hydrochloride (compare Brady and Dunn, T., 1916, **109**, 667).

The apparent failure of this method in the case of the hydrazones is not altogether surprising as, if the mechanism of the conversion of the *anti*- to the *syn*-oxime through the hydrochloride is along the lines indicated by Dunn and one of us (*ibid.*, p. 663), stereoisomeric change would not be expected in the case of the hydrazones under the same conditions.

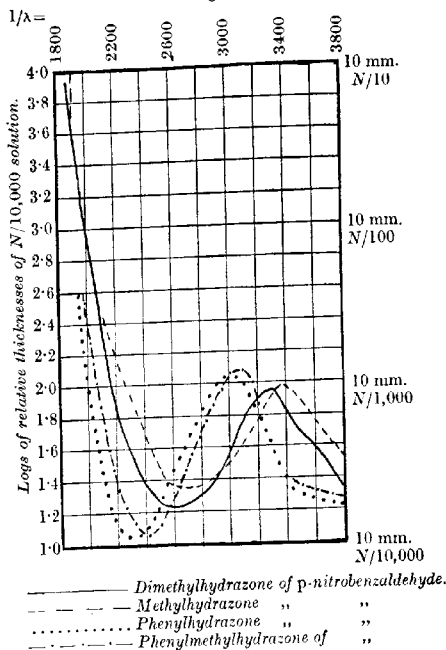
Attempts to prepare isomerides by the action of acetic anhydride (compare Thiele and Pickard, *Ber.*, 1898, **31**, 1249; Lockemann and Lucius, *loc. cit.*) were unsuccessful, the dimethylhydrazones being unchanged and the methylhydrazones giving an acetyl derivative.

Although the suggestion that the hydrazones undergo isomeric change to azo-compounds first made by Chattaway (T., 1906, **89**, 462) and supported by Baly and Tuck (*ibid.*, p. 982) seems to have been disposed of by the work of Stobbe and Nowak (*Ber.*, 1913, **46**, 2887), Busch and Dietz (*Ber.*, 1914, **47**, 3277), and Busch and Kunder (*Ber.*, 1916, **49**, 2345), it seemed of interest, while these compounds were available, to place on record their absorption spectra (Fig. 1). These closely resemble the absorption spectra of the corresponding phenyl- and phenylmethyl-hydrazones given by Baly and Tuck (*loc. cit.*) and here reproduced for comparison.

## EXPERIMENTAL.

*Benzaldehydediethylhydrazone*.—One gram of diethylhydrazine in alcoholic solution was added to 1.2 grams of benzaldehyde, and the mixture left over-night. On dilution, a yellow oil separated; this was extracted with ether, the solution washed with sodium bisulphite solution to remove unchanged aldehyde, dried, and the

Fig. 1.



ether removed, when the diethylhydrazone was obtained as a yellow, uncrystallisable oil. On treatment in dry ethereal solution with hydrogen chloride, an uncrystallisable hydrochloride was precipitated which, on decomposition with sodium carbonate solution, regenerated an oil. The addition of platinic chloride to a solution of the hydrazone in dilute hydrochloric acid precipitated a crystalline platinichloride which, after crystallisation from alcohol, was analysed (Found: Pt = 25.4.  $C_{22}H_{34}N_4Cl_6Pt$  requires Pt = 25.6 per cent.).

*p*-Nitrobenzaldehydediethylhydrazone.—Two grams of diethylhydrazine in alcohol were added to 3 grams of *p*-nitrobenzaldehyde in the same solvent. On treating as above, the hydrazone was obtained as a red oil. This was dissolved in ether and the solution saturated with hydrogen chloride, when a hydrochloride was precipitated as a yellow, crystalline powder (Found: Cl = 13.4.  $C_{11}H_{16}O_2N_3Cl$  requires Cl = 13.8 per cent.).

Decomposition of this hydrochloride with sodium carbonate solution regenerated a red oil. A solution of the hydrazone in dilute hydrochloric acid gave with platinic chloride a buff-coloured precipitate, which separated from alcohol as a buff-coloured, crystalline powder (Found: C = 31.0; H = 3.6; Pt = 22.7.  $C_{22}H_{32}O_4N_6Cl_6Pt$  requires C = 31.0; H = 3.8; Pt = 22.9 per cent.).

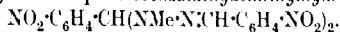
*m*-Nitrocinnamaldehydediethylhydrazone.—This compound, prepared in an analogous manner to the above, was obtained as a red oil. Its platinichloride separated from alcohol as a yellow, crystalline substance (Found: C = 34.0; H = 4.3; Pt = 21.6.  $C_{26}H_{36}O_4N_6Cl_6Pt$  requires C = 34.5; H = 4.0; Pt = 21.6 per cent.).

*p*-Nitrobenzaldehydedimethylhydrazone.—Two grams of dimethylhydrazine and 4 grams of *p*-nitrobenzaldehyde were mixed in alcoholic solution. After leaving over-night, the solution was diluted somewhat with water, when the hydrazone was precipitated as a yellow solid, which crystallised from alcohol in orange-yellow plates melting at  $111^\circ$  (Found: N = 22.0.  $C_9H_{11}O_2N_3$  requires N = 21.8 per cent.).

The *p*-nitrobenzaldehydedimethylhydrazone was dissolved in dry ether and the solution saturated with hydrogen chloride, when a yellow, crystalline hydrochloride was precipitated (Found: Cl = 15.2.  $C_9H_{12}O_2N_3Cl$  requires Cl = 15.5 per cent.).

This, on decomposition with sodium carbonate solution, regenerated the original hydrazone. The hydrazone was added to four times its weight of acetic anhydride, and a trace of concentrated sulphuric acid introduced. The hydrazone dissolved, but on decomposition of the anhydride with iced water the original dimethylhydrazone was regenerated.

*p*-Nitrobenzylidenebis-*p*-nitrobenzaldehydemethylhydrazone,



—Five grams of methylhydrazine sulphate were dissolved in the minimum amount of water, and an equimolecular amount of sodium hydroxide in a small quantity of water was added. Alcohol was then slowly added to the solution with vigorous stirring, when the bulk of the sodium sulphate crystallised out.



The alcoholic solution of methylhydrazine thus obtained was added to an alcoholic solution of 5 grams of *p*-nitrobenzaldehyde, and the mixture left over-night. On diluting, a yellow precipitate was obtained, which crystallised from alcohol in radiating clusters of orange-yellow needles melting at  $189^{\circ}$  (Found: N = 20.3.  $C_{23}H_{21}O_6N_7$  requires N = 20.0 per cent.).

*p*-Nitrobenzaldehydemethylhydrazone.—Twelve grams of methylhydrazine sulphate were treated as above, and the solution of methylhydrazine added to 4 grams of *p*-nitrobenzaldehyde in alcohol. On leaving over-night and diluting, the hydrazone was precipitated; it separated from alcohol as an orange-yellow, crystalline powder melting at  $93^{\circ}$  (Found: N = 23.6.  $C_8H_9O_2N_3$  requires N = 23.5 per cent.).

The hydrazone, on treatment in ethereal solution with hydrogen chloride, gave a precipitate of a hydrochloride which, on decomposition with sodium carbonate solution, regenerated the original methylhydrazone. It is rather remarkable that this compound is not converted into the *p*-nitrobenzylidenebis-*p*-nitrobenzaldehydemethylhydrazone by acids in an analogous manner to the conversion of the hydrazones into the azines.

*Acetyl-p*-nitrobenzaldehydemethylhydrazone.—The above methylhydrazone was added to four times its weight of acetic anhydride, cooled in ice, followed by one drop of concentrated sulphuric acid. The hydrazone dissolved, and on decomposing the excess of acetic anhydride with ice-water the acetyl derivative separated; it was crystallised from acetic acid and obtained in colourless prisms melting at  $186^{\circ}$  (Found: N = 19.2.  $C_{10}H_{11}O_3N_3$  requires N = 19.0 per cent.).

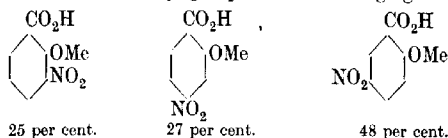
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# CXCVII.—*The Nitro- and Amino-Derivatives of o- and p-Methoxybenzoic Acids and of $\alpha$ - and $\beta$ -Methoxynaphthoic Acids.*

By VICTOR FROELICHER and JULIUS BEREND COHEN.

IN a former paper (T., 1921, 119, 1425), a series of nitro- and amino-derivatives of *m*-methoxybenzoic acid was prepared. An attempt has been made to apply similar methods to the preparation of the nitro- and amino-derivatives of *o*- and *p*-methoxybenzoic acids and of  $\alpha$ - and  $\beta$ -methoxynaphthoic acids.

Most of the isomeric nitro-compounds of the former two acids have already been described. They have generally been obtained by direct nitration of the hydroxy- and conversion into the methoxy-derivative. It was therefore of some interest to determine the orientation of the nitro-groups in the methoxy-acids. We found that it followed Holleman's rule, mentioned in our last paper. For example, the influence of the carboxyl group in determining the meta-orientation of the nitro-group was shown in the nitration of *o*-methoxybenzoic acid. The nitro-group entered mainly the meta-position to the carboxyl group, as the following figures show :



This is also in accordance with the investigations of Simonsen and Rau (T., 1917, **111**, 224), who showed that the orienting influence of a positive group (methoxyl) becomes very feeble when this group is accompanied by a negative (carboxyl) group in the ortho- or para-position.

The above-mentioned nitro-compounds as well as two of the corresponding amino-compounds have already been prepared by Simonsen and Rau (*loc. cit.*). They oxidised 3-, 4-, and 5-nitro-*o*-tolyl methyl ethers with permanganate and obtained the corresponding nitro-acids. These nitro-compounds were reduced to amino-compounds with ferrous hydroxide, a method which was not found satisfactory, the reduction with stannous chloride yielding better results. The 3-nitro-acid was also obtained by Störmer (*Ber.*, 1911, **45**, 655) by oxidation of the aldehyde, and by Fishman (*J. Amer. Chem. Soc.*, 1920, **42**, 2296) by oxidation of 3-nitro-2-methoxybenzyl alcohol. The 5-nitro-acid was obtained by Simonsen and Rau by diazotising 5-nitro-3-amino-2-methoxybenzoic acid and decomposing the diazo-compound and also by direct nitration (*loc. cit.*). Hale and Robertson (*Amer. Chem. J.*, 1908, **39**, 680), Kraut (*Annalen*, 1899, **150**, 6), and Salkowski (*ibid.*, 1894, **173**, 41), prepared the 4-nitro-compound (m.p. 148–150°), which they mistook for the 5-nitro-compound. The method of formation of the 5-nitro-acid (m. p. 161°) according to Simonsen and Rau offers a sufficient proof of its constitution. The main product obtained by us by nitrating the *o*-methoxy-acid had the m. p. 161° and was identical with the above, and when reduced yielded the same 5-amino-compound described by Simonsen and Rau. According to Holleman's theory, which is in agreement with

our own experience, the entrant nitro-group must yield the 5-nitro derivative.

When *p*-methoxybenzoic acid was nitrated, only one of the two possible nitro-compounds was obtained, the nitro-group entering the meta-position to the carboxyl group. It was found to be identical with the compound of m. p. 189° mentioned by Simonsen and Rau in their paper, but not further investigated by them. The preparation of the methoxybenzoic acids was carried out according to Cohen and Dudley (T., 1910, 97, 1739), and a satisfactory yield was obtained, but the preparation of  $\alpha$ - and  $\beta$ -methoxynaphthoic acids by the same method was found to give a very poor yield and was accordingly modified. The carboxyl group in these two compounds is very easily removed (Nietzki and Guitermann, *Ber.*, 1887, 20, 1274).

A small amount of  $\alpha$ -methyl 1-methoxy-2-naphthoate could be obtained by dissolving  $\alpha$ -naphthol-2-carboxylic acid in hot methyl sulphate and introducing the theoretical amount of a concentrated aqueous solution of sodium hydroxide as quickly as possible; but the reaction is too vigorous to be employed on a large scale. When sodium hydroxide was slowly introduced, a continuous evolution of carbon dioxide occurred and the solution then contained  $\alpha$ -naphthol and its methyl ether. The yield of methyl 1-methoxy-2-naphthoate could be greatly improved by first preparing the methyl  $\alpha$ -naphthol-2-carboxylate by the action of methyl sulphate on  $\alpha$ -naphthol-2-carboxylic acid in sodium carbonate solution. The yield of ester was 48 per cent., the unchanged acid being easily recovered. The ester was then methylated by dissolving it in methyl sulphate and introducing a large excess of sodium hydroxide solution.  $\beta$ -Naphthol-1-carboxylic acid was much more easily esterified; for when boiled with methyl alcohol and sulphuric acid, an almost theoretical yield of ester was obtained. This was converted into the methoxy-ester by the method mentioned above and gave a satisfactory yield.

The  $\alpha$ - and  $\beta$ -methoxy-naphthoic acids prepared by Cohen and Dudley (*loc. cit.*) were not quite pure. The melting points (120–123°; 126–130° respectively), first observed were the same, but, on conversion into the potassium salts and crystallisation, the acids were obtained in a purer state and showed somewhat higher melting points.

1-Methoxy-2-naphthoic acid gave, when nitrated, only one nitro-derivative, namely, 4-nitro-1-methoxy-2-naphthoic acid. Its constitution was determined as follows: When it was boiled for some minutes with strong hydriodic acid, a compound of m. p. 214° was obtained which was identical with 4-nitro-1-hydroxy-2-naphthoic

acid prepared by König (*Ber.*, 1890, 23, 807) and by Day (*T.*, 1915, 107, 1625), who determined its constitution by converting it into 4-nitro- $\alpha$ -naphthol. When nitromethoxynaphthoic acid was boiled for some time with hydriodic acid, the methyl group was removed and the nitro-group reduced, forming 4-amino-1-hydroxy-2-naphthoic acid. The same compound was also prepared by reduction of the above nitro-hydroxy-acid with stannous chloride. The 4-amino-hydroxy-2-naphthoic acid was prepared by Nietzki and Guitermann (*Ber.*, 1887, 20, 1274), by the action of benzenediazonium chloride on 1-hydroxy-2-naphthoic acid and reduction of the resulting azo-compound, and by Weil and Heerdt (*Ber.*, 1922, 55, [B], 224), by the action of diazotised sulphanilic acid on 1-hydroxy-2-naphthoic acid and reduction of the azo-compound thus formed. 4-Amino-1-methoxy-2-naphthoic acid obtained by reduction of the nitro-compound with stannous chloride does not form a tin salt (see also Weil and Heerdt, *loc. cit.*), but the hydrochloride, which is less soluble in water than the free amino-compound, separates from the solution.

The nitration of 2-methoxy-3-naphthoic acid yielded a mixture of nitro-derivatives which could not be separated by any of the usual methods. Owing to the high temperature required and the consequent decomposition of the product, the reduction could not be effected in the ordinary way. An attempt to reduce the nitro-compounds with stannous chloride dissolved in glacial acetic acid and saturated with hydrogen chloride gave the desired result. The reduction takes place in the cold. A tin salt was formed which, when treated with hydrogen sulphide, gave the hydrochloride of 6-amino-2-methoxy-3-naphthoic acid. Its constitution was determined as follows: when boiled with hydriodic acid, a compound of m. p. 230–232° was obtained, which on heating for some time with dilute sulphuric acid, yielded the 2:6-dihydroxy-3-naphthoic acid prepared by Schmid (*Ber.*, 1893, 26, 1118) by the action of caustic potash on 6-sulpho-2-hydroxy-3-naphthoic acid (D.R.-P. 69357, Friedländer, III, 506):



The amino-group in 6-amino-2-methoxy-3-naphthoic acid is not removed when treated in the same way with sulphuric acid, but the acetyl derivative is easily decomposed: and the resulting compound showed no sign of any amino-group being present. Although the replacement of the amino-group by hydroxyl has not been definitely ascertained, the new product has a different melting-point from that of the original methoxy-acid.

## EXPERIMENTAL.

*Nitration of the Methoxybenzoic Acids.*—Fifty grams of *o*-methoxybenzoic acid were dissolved in 500 c.c. of acetic anhydride and cooled in a freezing mixture. A mixture of 25 grams of fuming nitric acid and three times its volume of sulphuric acid was very slowly introduced and well stirred, and the temperature kept at  $-5^{\circ}$  to  $-8^{\circ}$ . The mixture was kept over-night, then poured on to ice, and filtered. The solid was recrystallised from glacial acetic acid and yielded two different nitro-compounds, the 3-nitro-acid of m. p.  $194-196^{\circ}$  being less soluble than the 4-nitro-compound of m. p.  $147-149^{\circ}$ . The mother-liquor, on evaporation, deposited the 5-nitro-compound, which is more soluble in glacial acetic acid than the other isomerides.

*p*-Methoxybenzoic acid, owing to its insolubility, was nitrated in suspension in acetic anhydride. Only one nitro-compound was obtained; 10 grams of methoxy-acid gave 7.8 grams of 3-nitro-4-methoxybenzoic acid of m. p.  $189-190^{\circ}$ . It crystallises from glacial acetic acid in pale yellow needles which are insoluble in alcohol (Found: N = 6.99.  $C_9H_7O_5N$  requires N = 7.10 per cent.).

*4-Amino-2-methoxybenzoic Acid.*—This acid was obtained by reduction of the corresponding nitro-compound with stannous chloride. It is soluble in hot water, from which it may be recrystallised. On heating, it slowly changed colour at about  $205^{\circ}$  and melts completely at  $217-218^{\circ}$  (Found: N = 8.24.  $C_8H_9O_3N$  requires N = 8.38 per cent.).

*3-Carbamido-4-methoxybenzoic Acid.*—3-Amino-4-methoxybenzoic acid was dissolved in hydrochloric acid and potassium cyanate added until alkaline. After boiling for some minutes, the product was filtered and washed with water. It is soluble in alcohol, benzene, light petroleum, or ether, but slightly soluble in hot water, from which it crystallises in colourless rosettes which melt at  $313^{\circ}$  with decomposition (Found: N = 13.58.  $C_9H_{10}O_4N_2$  requires N = 13.34 per cent.).

*3-Carboxy-amino-4-methoxybenzoic Acid.*—3-Amino-4-methoxybenzoic acid was dissolved in sodium carbonate solution and chloroformic ester added. After heating for some minutes on the water-bath, the solution was allowed to cool, acidified with hydrochloric acid, and filtered. The product is slightly soluble in water and soluble in alcohol. It was crystallised from dilute alcohol and formed colourless needles, m. p.  $227-228^{\circ}$  (Found: N = 5.98.  $C_{11}H_{13}O_5N$  requires N = 5.85 per cent.).

*1-Methoxy-2-naphthoic Acid.*—Thirty grams of 1-naphthol-2-carboxylic acid were dissolved in 200 c.c. of 10 per cent. sodium carbonate solution and 12 grams of methyl sulphate slowly intro-

duced. The mixture was heated on the water-bath and shaken from time to time. After half an hour, the brown precipitate was filtered, washed with cold water, and dried. The yield was 7.5 grams and the m. p.  $75-80^{\circ}$ . When the same experiment was repeated with more methyl sulphate, the yield was raised to 48 per cent. This reaction did not take place when caustic soda was used instead of sodium carbonate, as the ester is readily hydrolysed by very dilute sodium hydroxide solution.

Ten grams of the ester were dissolved in 18.6 grams of methyl sulphate and heated at about  $120^{\circ}$  until all was dissolved. Through the top of the reflux condenser 6 grams of sodium hydroxide, dissolved in an equal amount of water, were introduced. A vigorous reaction occurred, which soon ceased. After boiling for two hours, the product was allowed to cool and poured into water which was rendered slightly alkaline. The oil (methyl-ester) which separated was extracted with ether, the ethereal solution dehydrated, and the ether removed. The oil was then hydrolysed with alcoholic potash. The methoxy-acid was obtained in brown crystals which melted at  $121-124^{\circ}$  (8.4 grams). It could be purified by converting it into the potassium salt, which was twice recrystallised from dilute alcohol. The pure methoxy-acid melts at  $126-128^{\circ}$  and crystallises from alcohol in colourless needles (Found: C=70.95; H=5.12. Calc., C=71.28; H=4.95 per cent.).

*2-Methoxy-1-naphthoic Acid*.—The ester was prepared very good in yield according to Cohen and Dudley (*loc. cit.*). It was converted into methoxynaphthoic acid in the same manner as described above.

Twenty grams of  $\beta$ -naphthol-1-carboxylic acid gave 14.4 grams of methoxynaphthoic acid, or 72 per cent. It crystallises from alcohol in colourless prisms, m. p.  $126-130^{\circ}$ , but after recrystallisation of the potassium salt from dilute alcohol the pure methoxy-acid melts at  $133-134^{\circ}$  (Found: C=70.95; H=5.18. Calc., C=71.28; H=4.95 per cent.).

*4-Nitro-1-methoxy-2-naphthoic Acid*.—Methoxynaphthoic acid was nitrated in the manner already described. Ten grams of the acid yielded 8.7 grams of crude nitro-acid, or, after recrystallisation from glacial acetic acid, 6.0 grams of acid, m. p.  $195-196^{\circ}$  (Found: N=5.52;  $C_{12}H_9O_3N$  requires N=5.66 per cent.). It is insoluble in water or benzene, but soluble in alcohol or hot acetic acid, from which it crystallises in pale yellow, silky leaflets.

*4-Nitro-1-hydroxy-2-naphthoic acid* was prepared by boiling 1 gram of the nitromethoxy-acid for two minutes with strong hydriodic acid. On standing over-night, a crystalline compound (yellow needles) separated which had m. p.  $214^{\circ}$ .

*4-Amino-1-methoxy-2-naphthoic Acid.*—Eight grams of the nitro-compound were reduced with stannous chloride, from which the hydrochloride was precipitated free from tin. On dissolving in sodium carbonate solution and precipitating with acetic acid, the free amino-compound was obtained. It melts with decomposition at 190–191° (4 grams). It is not soluble in cold alcohol, water, glacial acetic acid, or benzene, but is slightly soluble in hot water, from which it crystallises in pale brown needles (Found: N = 6.25.  $C_{12}H_{11}O_3N$  requires N = 6.45 per cent.).

*4-Carbamido-1-methoxy-2-naphthoic Acid.*—The dry hydrochloride of 4-amino-1-methoxy-2-naphthoic acid was heated with a solution of potassium cyanate in water for some minutes on the water-bath. The precipitate was filtered when cold and washed with water. It is slightly soluble in hot water or benzene, soluble in alcohol or glacial acetic acid, and fairly soluble in ether. It darkens at 170° and melts at 176–177° with decomposition (Found: N = 10.58.  $C_{13}H_{12}O_4N_2$  requires N = 10.77 per cent.).

*4-Carboethoxyamino-1-methoxy-2-naphthoic Acid.*—The hydrochloride of 4-amino-1-methoxy-2-naphthoic acid was dissolved in a 10 per cent. aqueous solution of potassium carbonate and shaken with chloroformic ester. After being warmed on the water-bath for a few minutes the precipitate was filtered. It is insoluble in water, fairly soluble in ether, and soluble in hot glacial acetic acid, from which it may be crystallised. It melts at 210° with decomposition (Found: N = 5.30.  $C_{15}H_{15}O_5N$  requires N = 5.51 per cent.).

*6-Amino-2-methoxy-3-naphthoic Acid.*—The mixture of nitro-2-methoxy-3-naphthoic acids (27 grams) was treated in the cold with a 25 per cent. solution of stannous chloride in glacial acetic acid which was saturated with hydrogen chloride. The reaction began immediately, and was completed by warming on the water-bath for a quarter of an hour; the tin salt separated on cooling. The rest of the tin salt, dissolved in the mother-liquor, was obtained by concentrating and saturating with hydrogen chloride. The precipitate was dissolved in hot water, and hydrogen sulphide passed in until all the tin was precipitated. The filtrate was concentrated by boiling it in a flask fitted with a Bunsen valve to prevent oxidation. The hydrochloride separated in long, brown needles (13 grams). It was converted, by treating it with a concentrated solution of sodium acetate, into the free amino-compound, which crystallises from pyridine in glistening leaflets, m. p. 310°, is soluble in water, alcohol, glacial acetic acid, or hot pyridine, but insoluble in ether or benzene (Found: N = 6.38.  $C_{12}H_{11}O_3N$  requires N = 6.45 per cent.).

The amino-compound is easily diazotised and then gives red azo-colours with  $\alpha$ - and  $\beta$ -naphthols and resorcinol. The *sulphate* crystallises from alcohol in long, yellow needles which melt at  $196^{\circ}$ . It is less soluble in water than the free amino-compound.

The *acetyl* derivative was obtained by boiling the amino-compound with acetic anhydride and sodium acetate for two hours. When the resulting solution was concentrated, the acetyl derivative separated. It is soluble in alcohol or glacial acetic acid, slightly soluble in ether or benzene, but insoluble in water. It crystallises from dilute alcohol in slightly brown, short prisms which melt sharply at  $193^{\circ}$ . When heated on the water-bath for one hour with a 4 per cent. solution of sulphuric acid, a colourless precipitate was obtained on cooling, which, after being recrystallised from dilute alcohol, melted at  $240-241^{\circ}$ . It is soluble in hot alcohol, but insoluble in water. It cannot be diazotised and does not form any salts with mineral acids. It is probably 6-hydroxy-2-methoxy-3-naphthoic acid.

*6-Amino-2-hydroxy-3-naphthoic Acid.* — 6-Amino-2-methoxy-3-naphthoic acid was heated on the water-bath for half an hour with a 20 per cent. solution of hydriodic acid. On cooling, yellow needles separated which were filtered and converted into the free amino-compound by the addition of sodium acetate. The hydroxy-acid is soluble in alcohol, ether, or ethyl acetate, but slightly soluble in hot water, benzene, or chloroform, and insoluble in light petroleum. Recrystallised from dilute alcohol, it forms long, pale yellow needles or rosettes which partly decompose above  $210^{\circ}$ , finally melting at  $230-232^{\circ}$ . It gives a red colour with very dilute ferric chloride and a green colour with sulphuric acid. It is easily diazotised, and then gives a red azo-colour with  $\alpha$ - and  $\beta$ -naphthols and resorcinol (Found:  $N=7.07$ .  $C_{11}H_9O_3N$  requires  $N=6.89$  per cent.).

When boiled for seven hours with a 4 per cent. solution of sulphuric acid and then evaporated to a small volume, a yellow precipitate was obtained which, after being recrystallised from dilute alcohol, melted at  $227-228^{\circ}$  and showed all the properties of 2:6-hydroxy-3-naphthoic acid.

*6-Carbamido-2-methoxy-3-naphthoic Acid.* — The hydrochloride of 6-amino-2-methoxy-3-naphthoic acid was heated with a concentrated solution of potassium cyanate on the water-bath for some minutes. When cold, the liquid was acidified with hydrochloric acid, and the precipitate filtered and washed with water. It is soluble in alcohol, slightly soluble in hot water, but insoluble in ether, benzene, chloroform, or light petroleum. When recrystallised from dilute alcohol, it melts at  $215-216^{\circ}$  (Found:  $N=10.59$ .  $C_{13}H_{13}O_4N_2$  requires  $N=10.76$  per cent.).



*6-Carbamido-2-hydroxy-3-naphthoic Acid*.—This compound was prepared in the same manner as described above and recrystallised from water. It is soluble in alcohol, pyridine, or hot water, but insoluble in ether or benzene. It began to darken at 200° and melted at 340–341° (Found: 11.35.  $C_{12}H_{10}O_4N_2$  requires N = 11.38 per cent.).

Attempts to prepare the carbethoxyamino-derivative by the action of chloroformic ester on the amino-group gave a sticky mass which could not be crystallised.

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[Received, July 5th, 1922.]

### CXCVIII.—*Studies of the Glucosides. Part I. The Constitution of Indican.*

By ALEXANDER KILLEN MACBETH and JOHN PRYDE.

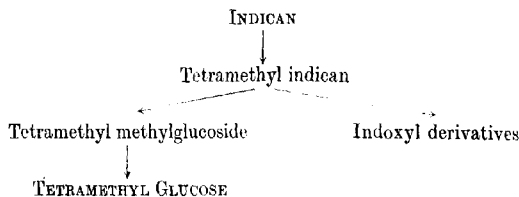
THE study of the constitution of a glucoside must, to be exhaustive, take into account three main points. In the first place, the constituent sugar and the group with which it is combined must be identified, and the actual union of these components must be determined: this may be deduced from an examination of the products obtained by hydrolysis, either by dilute acid or the action of an enzyme, but when the non-sugar residue contains several hydroxyl groups the structure arrived at by such considerations is open to some doubt. In the second place, the particular configuration of the glucoside must be determined, for the compound may exist in the  $\alpha$ - and  $\beta$ -stereoisomeric forms: this question may generally be settled by the study of enzyme action, for, since emulsin is the specific enzyme for  $\beta$ -alkyl glucosides it may reasonably be concluded that all glucosides hydrolysed by it are derived from  $\beta$ -glucose. The question now remaining to be dealt with is connected with the nature of the sugar residue. Modern conceptions of the structure of the sugars (Fischer, *Ber.*, 1914, 47, 1980; Irvine, Fyfe, and Hogg, *T.*, 1915, 107, 524; Irvine and Robertson, *T.*, 1916, 109, 1305) show that the simple sugars and their derivatives may exist in modifications other than the ordinary butylene-oxide type: the internal linking of the sugar molecule in the natural glucosides therefore becomes a matter of prime importance. Trustworthy information on this point cannot be obtained from a study of the sugar resulting from the hydrolysis of the simple glucoside, for rearrangement of the free hydroxyl groups of the carbohydrate

may occur during this process. Inulin, for example, on hydrolysis yields fructose of the butylene-oxide type, whereas trimethyl inulin, in which the possibility of any internal rearrangement is excluded, is hydrolysed to a methylated  $\gamma$ -fructose (Irvine and Steele, T., 1920, **117**, 1474; see also this vol., p. 1060). Sucrose, moreover, on direct hydrolysis yields glucose and fructose, both of which possess the butylene-oxide linking: but octamethyl sucrose is hydrolysed to a tetramethyl glucose of the butylene oxide series and a methylated  $\gamma$ -fructose (Haworth and Law, T., 1916, **109**, 1314). It seems clear, therefore, that trustworthy information regarding the internal structure of the sugar constituent of the natural glucosides may most readily be obtained by a study of the products of hydrolysis of the alkyl derivatives of these compounds; the actual hydroxyl group involved in glucoside formation may also be determined by such methods, when the non-sugar residue is a substance containing several such groups. It is proposed to undertake such work in this series of papers, and it is hoped to supplement the results thus obtained by direct synthesis of the glucosides themselves.

The alkylation of the glucosides has already received some attention. Irvine and Rose (T., 1906, **89**, 814) prepared a pentamethyl salicin from the natural glucoside and showed that the sugar in the parent glucoside possessed a butylene-oxide linking. They supported these observations by a synthesis of a pentamethyl salicin which proved to be identical with that derived from the natural glucoside by methylation. Moore and Tutin (T., 1910, **97**, 1285) applied the methylation process to gynocardinic acid derived from the natural glucoside gynocardine. A pentamethylgynocardinate was obtained, but no attempt seems to have been made to isolate the methylated sugar.

Although indican has been isolated as the glucoside from *Isatis tinctoria*, *Polygonum tinctorium*, and other plants by Schunck (Phil. Mag., 1855, [iv], **10**, 74; 1858, [iv], **15**, 127), the correct formula was not established until many years afterwards (Marchlewski and Radcliffe, J. Soc. Chem. Ind., 1898, **17**, 434). The latter workers showed that the glucoside had the composition  $C_{14}H_{17}O_6N$ , and gave on hydrolysis glucose and indoxyl, the latter being converted into indigotin on oxidation. Subsequent workers confirmed the observation that indican was an indoxyl glucoside, and indicated that the constituent sugar was *d*-glucose. Ter Meulen (Rec. trav. chim., 1905, **24**, 444), established the nature of the component sugar by a method in which he made use of the fact that an enzyme enters into combination only with a sugar the simple glucosides of which it is able to hydrolyse. Examining the rate of

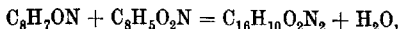
hydrolysis of indican by the indigo-enzyme in the presence of different sugars, he found that *d*-glucose was the only sugar which appreciably retarded the speed of the reaction. It may reasonably be deduced from this that *d*-glucose is the component sugar of this glucoside. This deduction was supported by isolating a crystalline sugar from the glucoside, and examining its properties. A. G. Perkin and his collaborators have also examined the sugar prepared from crystalline indican (T., 1905, 91, 1715) and found it to be *d*-glucose. Substantial proof, therefore, has been submitted that the sugar isolated from indican is *d*-glucose, but no evidence regarding the internal linking of the sugar has been adduced. The work described in this paper may be outlined in the following scheme:



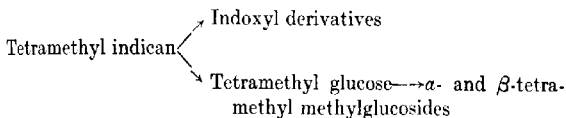
If the sugar residue in indican possesses the normal butylene-oxide structure, the tetramethyl glucose isolated from it should be the well-known 2 : 3 : 5 : 6-compound, which is crystalline and may be readily identified. If any alternative linking is present in the constituent sugar, an isomeric tetramethyl glucose would result, from which the structure of the sugar molecule might be deduced.

As only 5 grams of indican were available, it was decided to methylate the compound by the action of methyl iodide and dry silver oxide, instead of by alternative methods in which a greater experimental loss might be expected. The methylation proceeded normally without oxidation occurring, but in the first stages it was found necessary to use a little methyl alcohol to bring about solution of the glucoside in methyl iodide. The product, isolated as described in the experimental part, was amorphous, and all attempts to obtain a crystalline material resulted in the formation of an oil, from which, on evaporation of traces of the solvent, the material was obtained in its original state as a friable glass. The tetramethyl indican isolated was easily soluble in most organic solvents, and had a low dextrorotation in acetone (+ 9.19°). It behaved as a normal methylated glucoside, and contained no traces of reducing sugars, indoxyl, or indigotin: it was accordingly submitted to hydrolysis.

Baeyer (*Ber.*, 1881, **14**, 1745) showed that indoxyl condenses with isatin to form indirubin,



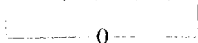
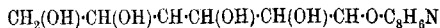
and this reaction has been employed for the characterisation of the indoxyl produced by the hydrolysis of indican (Beyerinck, *Proc. K. Akad. Wetensch., Amsterdam*, 1899, **2**, 120; Hazewinkel, *ibid.*, 1900, **2**, 512). Orchardson, Wood, and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 4) adopted Beyerinck's suggestion that the reaction might be quantitative and developed a method of estimation which has been tested with specimens of crystalline indican (Perkin, *loc. cit.*) and found to be trustworthy. On submitting tetramethyl indican to this reaction, indirubin was produced, but the yield was only about 50 per cent. of the theoretical. From this it is seen that indoxyl is produced by the hydrolysis of methylated indican, and therefore it may be concluded that the non-sugar part of the glucoside is not acted on during the methylation process. The low yield of indirubin is doubtless due to the slow rate at which the hydrolysis of the methylated indican proceeds; and it was on this account that, with the object of isolating the sugar residue, the main portion of the tetramethyl indican was not submitted to hydrolysis by dilute aqueous acids, but was subjected to the action of methyl alcohol containing 1 per cent. of hydrogen chloride. This method, which has previously been applied with success (Irvine and Rose, *loc. cit.*), results in the hydrolysis of the glucoside and the simultaneous formation of the corresponding methylglucosides according to the scheme



Schunck and Römer (*Ber.*, 1879, **12**, 2311) showed that the acid hydrolysis of indican in the absence of air gave rise to a product which did not yield indigotin when treated with oxidising agents. Perkin and Bloxam (*loc. cit.*) have supported this observation and made a further study of the hydrolysis of the glucoside by dilute acids. When air was excluded they obtained a substance for which they proposed the name *indoxyl brown*. This product is soluble in alcohol and insoluble in ether, being precipitated by the latter as an amorphous, brown powder from concentrated alcoholic solutions. During the hydrolysis of tetramethyl indican the alcohol darkened considerably, and after filtration and evaporation of the alcohol a resinous syrup was obtained. The methylated sugar was removed

from this by repeated extraction with ether, and an amorphous brown powder remained which closely corresponded with the indoxyl-brown described by Perkin.

The isolated sugar derivative was found to be tetramethyl methylglucoside, but traces of tetramethyl glucose which had escaped glucoside formation were also present. This was converted into the corresponding glucoside by methylation, and the product was found to consist of a mixture of the  $\alpha$ - and  $\beta$ -forms of tetramethyl methylglucosides possessing the ordinary butylene-oxide linking. On hydrolysis of these glucosides by aqueous acid, a crystalline tetramethyl glucose was isolated, which was readily identified as the 2:3:5:6- or butylene-oxide compound. From the results obtained it is evident that indican is derived from a molecule of *d*-glucose combined with indoxyl, the internal linking of the sugar being of the butylene-oxide type. The following structure is therefore established for the glucoside:



and enzyme action and optical properties indicate that the compound is a derivative of  $\beta$ -glucose.

In view of the results described in this paper, it is intended to attempt a synthesis of indican through the action of bromo-tetra-acetyl glucose on derivatives of indoxyl.

#### EXPERIMENTAL.

##### *The Methylation of Indican. Tetramethyl Indican.*

The starting material was 5 grams of triple recrystallised indican prepared in the Indigo Research Laboratories at Pusa, Bihar. This was methylated by the action of methyl iodide and dry silver oxide, coal gas being passed through the apparatus to minimise any tendency to oxidation during methylation. At no stage of the process was any development of the blue colour of indigotin observed. The following operations were carried out and the yield of methylated material after these five treatments was 4.83 grams:

<i>Extraneous solvent.</i>	<i>Reagents.</i>	<i>Extractive solvent.</i>
1. 20 c.c. Methyl alcohol.	32 grams $\text{Ag}_2\text{O}$	21.8 c.c. $\text{CH}_3\text{I}$ . Methyl alcohol.
2. 10 c.c. " "	32 " 17 " "	" "
3. 1 c.c. " "	24 " 25 " "	" "
4. Nil " "	24 " 25 " "	Ether "
5. Nil " "	16 " 14 " "	" "

The product from the final methylation gave, on removal of the ether, a yellow, non-deliquescent glass, which softened at about

100–110°, and was easily reduced to a fine powder. It was readily soluble in methyl or ethyl alcohol, acetone, methyl iodide, chloroform, ether, or ethyl acetate, slightly soluble in light petroleum, and insoluble in water. It was neutral in reaction and did not reduce Fehling's solution. After boiling with dilute hydrochloric acid, the reduction of Fehling's solution was very marked, and the behaviour of the compound was thus typical of a glucoside. The observed methoxy-content was lower than that calculated for a tetramethylindican. (Found: OMe = 32.4.  $C_8H_6ON \cdot C_6H_7O(OMe)_4$  requires OMe = 35.3;  $C_8H_6ON \cdot C_6H_8O_2(OMe)_3$  requires OMe = 27.6 per cent.)

The low figure for the methoxy-content is not due to incomplete methylation, for after subjecting the material to two further methylations the result was not appreciably altered. The low result is rather to be expected, for the methylated indican is resinified by hot hydriodic acid, and the methyl iodide is evolved much more slowly than is usual in methoxy-estimations; and to this resinification the low Zeisel value is doubtless due.

Attempts were made to crystallise the methylated indican from various solvents, but in all cases an oily product was obtained, from which, on the removal of the solvent, the methylated indican was again isolated as a friable glass. To effect purification the material was therefore extracted under reflux with light petroleum containing a little ethyl acetate. After removal of the main bulk of the solvent, the product was freed from the last traces by heating to 100° at a pressure of 10 mm. The tetramethyl indican was obtained as a yellow glass which gave the analytical figures quoted below, and further purification treatment did not materially affect the analytical results [Found: C = 60.9; H = 7.12; OMe = 32.13.  $C_{14}H_{13}O_2N(OMe)_4$  requires C = 61.5; H = 7.12; OMe = 35.3 per cent.]

The tetramethyl indican was further characterised by its rotatory power. In acetone, a low dextrorotation was observed.

$\alpha_D = +0.104^\circ$ ,  $l = 200$  cm.,  $c = 0.5657$ ; whence  $[\alpha]_D^{25} = +9.19^\circ$ .

On hydrolysis of the tetramethyl indican by aqueous hydrochloric acid in the presence of isatin, indirubin was formed, but the quantity obtained was less than 50 per cent. of the theoretical amount. 0.1038 Gram gave 0.0366 gram of indirubin. Theory requires 0.0797 gram of indirubin. The low result is doubtless due to the slow rate at which the hydrolysis proceeds, which is not an unexpected result in view of the insolubility of the methylated glucoside in aqueous media. A further quantity of indirubin slowly precipitates from the filtrates as hydrolysis proceeds, which is in accordance with the view expressed above.

*Simultaneous Hydrolysis and Condensation of Tetramethyl Indican.*

As already stated, it was decided to accomplish the hydrolysis of the methylated indican by the action of methyl-alcoholic solutions of hydrogen chloride, the component sugar being isolated from the reaction as the tetramethyl methylglucoside. Four grams of the methylated indican were accordingly dissolved in 60 c.c. of dry methyl alcohol containing 1 per cent. of hydrogen chloride, and the solution was heated in a sealed tube for twenty-four hours. The temperature of the furnace was kept at  $80^{\circ}$  for the first sixteen hours, and was then gradually raised to  $100^{\circ}$ , the latter temperature being maintained for a further seven hours. The solution darkened considerably during the reaction, and on cooling and opening the tube it was found that a small amount of a lustrous, black precipitate had been formed. The alcohol was filtered off, and the residue, after being washed with methyl alcohol, was found to contain nitrogen and is doubtless a complex condensation product of indoxyl. The filtrate was neutralised by silver carbonate, and after filtration and evaporation of the alcohol under reduced pressure a resinous syrup remained. This was deep carmine in colour, and after repeated extraction with boiling ether a considerable amount of a brown, amorphous powder remained, the properties of which were in accordance with Perkin's description of indoxyl-brown. The ethereal extract was coloured a deep carmine, which was probably due to the presence of an ether-soluble colouring matter derived from indoxyl. To eliminate this impurity from the methylated sugar, the ether was removed under reduced pressure, the residual syrup dissolved in water and the solution gently heated after the addition of a little vegetable charcoal (norit). This was found to be very effective, and the filtrate after this treatment showed only a pale golden-yellow colour. The water was removed from the filtrate by distillation under reduced pressure, and its last traces were eliminated by successively adding and distilling off small quantities of alcohol. The syrup was finally extracted with ether and the ethereal solution dried with anhydrous sodium sulphate. On filtering and removing the solvent, 2.1 grams of a mobile, pale yellow syrup were obtained.

The syrup was distilled under greatly reduced pressure and boiled at  $110-115^{\circ}/1.4$  mm.;  $n_D = 1.4498$ . [Found: OMe = 57.5. Tetramethyl methylglucoside ( $n_D = 1.4460$ ) requires OMe = 62.0. Tetramethyl glucose ( $n_D = 1.4583$ ) requires OMe = 52.6 per cent.]

From the refractive index of the product and its methoxy-content it was evident that it consisted principally of tetramethyl methyl-

glucoside mixed with a small amount of tetramethyl glucose which had escaped glucoside formation. This view was supported by the fact that the syrup had a slight reducing action on Fehling's solution. It was therefore thought advisable to complete the conversion into the glucoside by methylation with methyl iodide, and on extracting the product of this reaction with ether and removing the solvent, a clear, colourless syrup was obtained which had no reducing action. It had a methoxy-content of 61.2 per cent. and  $n_D$  1.4460. Conversion to the methylglucoside was therefore complete. The optical rotation of the product indicated that it contained an excess of the  $\alpha$ -form of tetramethyl methylglucoside.  $[\alpha]_D^{15}$  in water = +89.5°, which corresponds with a mixture of 65 per cent. of the  $\alpha$ -form ( $[\alpha]_D = +147.4^\circ$ ) with 35 per cent. of the  $\beta$ -form ( $[\alpha]_D = -17.34^\circ$ ).

*Hydrolysis of Tetramethyl Methylglucoside.*

The hydrolysis of the tetramethyl methylglucosides isolated from tetramethyl indican as described above was effected by boiling with 8 per cent. aqueous hydrochloric acid. 0.7392 Gram of the glucoside was dissolved in 43.5 c.c. of aqueous acid, and after the addition of a little vegetable charcoal the solution was boiled for thirty minutes over a wire gauze. The presence of a little charcoal during the hydrolysis of methylglucosides has been found to prevent the development of colour, which is a great advantage when following the course of the reaction polarimetrically. The calculated concentration of tetramethyl glucose resulting from hydrolysis in the above solution is 1.5904 per cent., and this should give an optical value of  $\alpha_D = +2.65^\circ$  with a 200 cm. tube (tetramethyl glucose equilibrium value in water  $[\alpha]_D = +83.3^\circ$ ). The  $\alpha_D$  observed after the hydrolysis had been proceeding for thirty minutes was +2.55°, and therefore at the end of this time the hydrolysis was complete. The solution was accordingly filtered and neutralised with barium carbonate. After another filtration, the water was distilled off under reduced pressure, and the dry residue extracted with boiling ether. On removing the solvent from the ethereal extract, a colourless syrup was obtained which on cooling began to crystallise in compact rosettes of needles. A portion of the syrup on nucleation with a specimen of 2:3:5:6-tetramethyl glucose, prepared by the direct methylation of glucose, immediately solidified.

The crystals obtained melted at 70°, and after one recrystallisation from light petroleum containing a little ethyl acetate the value had risen to 80°. Subsequent recrystallisation from light petroleum



raised the melting point to  $94^{\circ}$ , the change of the melting point on recrystallisation being characteristic of tetramethyl glucose.

The tetramethyl glucose showed the customary mutarotation in solvents, the optical change in water being from  $+91.5^{\circ} \rightarrow 83^{\circ}$ , which is in good agreement with the values already established for the compound. It is therefore established that the sugar resulting from methylated indican is tetramethyl glucose of the butylene-oxide type, and from this it follows that in the parent glucoside the component sugar possesses a linking of this type.

We wish to express our thanks to Mr. W. A. Davis of the Indigo Research Laboratories, Pusa, Bihar, for kindly supplying us with the indican used in the work ; to Principal Irvine, F.R.S., for the kindly interest he has taken in the work throughout its course, and to the Commissioners of the 1851 Exhibition for a scholarship which has made it possible for one of us to participate in the research.

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### CXIX.—*The Catalytic Decomposition of Formic Acid on Surfaces of Platinum and Silver.*

By HAROLD CALVERT TINGEY and CYRIL NORMAN HINSHELWOOD.

THE thermal decomposition of formic acid occurs in the following ways :



In each case the equilibrium lies almost completely on the side of the products of decomposition. The decomposition is very sensitive to catalytic influences, which determine not only the total velocity of the reaction, but also the relative ease with which the two alternative modes of change (a) and (b) take place. The study of the influence of conditions such as temperature and the nature of the catalyst on the reactions may be expected to yield information of some interest in connexion with the general theory of heterogeneous catalysis.

Hinschelwood, Hartley, and Topley (*Proc. Roy. Soc.*, 1922, [A], 100, 575) have found that on soda glass the two reactions proceed

at about equal rates in the neighbourhood of  $280^{\circ}$ , but that the temperature coefficients of velocity differ very considerably, the velocity of reaction (a) increasing about 1.7—1.8 times for  $10^{\circ}$  rise in temperature, and that of reaction (b) about 1.3—1.4 times. Interpreting the results in the light of the view that the velocity of a heterogeneous reaction is not governed by the velocity of diffusion through an adsorbed layer of considerable thickness, but that the observed velocity is that of a chemical change in a unimolecular layer on the surface of the catalyst, the conclusion is drawn that a molecule which reacts must not only possess a minimum critical energy, according to the accepted view, but must also be in a certain phase. Otherwise two reactions associated with such different temperature coefficients and correspondingly different critical energies could not proceed at roughly equal rates at the same temperature.

- The object of the experiments to be described was to study the influence of temperature on the two reactions on catalytic surfaces of silver and platinum, in order to ascertain whether the behaviour of the formic acid on these catalysts is analogous to its behaviour on glass. The problem is rendered more difficult by the extreme variability of the catalytic surfaces, and special devices have had to be adopted to obtain the desired information about temperature coefficients.

The results are briefly as follows. On platinum, from  $235^{\circ}$  down to  $80^{\circ}$ , reaction (a) yielding carbon dioxide and hydrogen predominates almost exclusively. As the reaction on platinum at  $80^{\circ}$  is proceeding much more slowly than it does on glass at temperatures where reaction (b) greatly predominates, the behaviour on platinum is not analogous to that on glass. The temperature coefficient of the reaction on platinum is, however, approximately the same as that of the corresponding reaction on glass, 1.7—1.8, the "heat of activation" being 22,000 cals. per gram-molecule, whilst that for glass is 28,000.

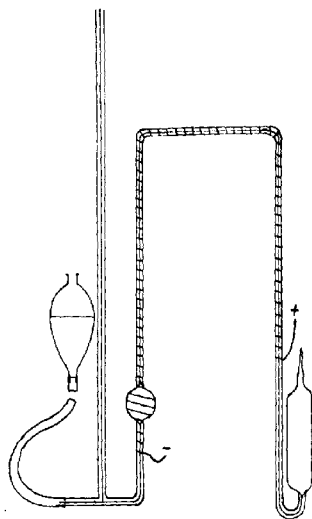
On silver, the main reaction taking place is that yielding carbon dioxide and hydrogen. Although varying amounts of carbon monoxide are found in the reaction products, some of this may be attributed to the reaction taking place on the glass reaction bulb; it is, however, doubtful whether all the carbon monoxide formed can be thus accounted for. The temperature coefficient for the carbon dioxide reaction is again high, as on glass and platinum, being 1.9 from one series of experiments and 2.3 from another series, over a different range of temperature. These give a mean heat of activation of 31,000 cals.

It was necessary to investigate the possibility of disturbances

in the composition of the products of reaction due to the secondary reaction,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , where the equilibrium lies well on the carbon dioxide side at the temperature of the experiments. It was concluded that the results could not be appreciably influenced by this.

*Methods and Apparatus.*—The reaction velocities were measured by two methods: (a) by measuring manometrically the increase in pressure which accompanies the decomposition, (b) by measuring volumetrically the gases produced in a known time from a known weight of acid heated in a sealed bulb.

FIG. 1.



(a) *Manometric Experiments.*—The apparatus used was a cylindrical bulb about 4 cm. long and 1.5 cm. in diameter, the lower end of which was sealed to a capillary tube of fine internal bore about 40 cm. long and bent so as to communicate through a mercury reservoir with a manometer and levelling tube (see Fig. 1).

This capillary, which was kept at a temperature of 135–150° by a suitable, electrically-heated winding of nichrome wire from the reaction bulb to beyond the mercury reservoir, served to transmit the pressure in the bulb to the mercury surface without allowing mercury or its vapour to reach the catalyst. To fill the bulb with formic acid vapour, a large excess was boiled off from it at a

temperature 10–30° below the reaction temperature, by heating in a constant-temperature air-bath. The tip was then sealed off and the bulb transferred to the thermostat before condensation could occur.

Constant temperatures were maintained by vapour baths of boiling liquids in which the reaction bulb was immersed.

(b) *Sealed Bulb Experiments*.—The bulbs were of soda glass, cylindrical, of about 15 c.c. volume. A suitable amount of acid, in a fragile, sealed capillary, was introduced. The bulb was evacuated to below 1 mm. pressure, and sealed off, the capillary containing the acid being then broken. After heating, the volume and the composition of the gaseous products were determined.

In calculating velocity constants, allowance was always made for differences in the volume of the various bulbs, since the observed velocity constant is directly proportional to the area of the catalytic surface and inversely to the volume of the bulb.

(c) *Analysis of Gases*.—Samples of reaction products were drawn off into an evacuated gas pipette and transferred to a Haldane gas analysis apparatus.

(d) *Experiments on the Water Gas Equilibrium*.—In these experiments carbon monoxide at 0.5–1 atmosphere pressure was sealed up with excess of water in glass bulbs containing the catalyst, the bulb heated in an electric furnace, and the products were analysed.

(e) *Preparation and Treatment of Catalysts*.—Much difficulty was found in preparing and preserving catalysts which would yield constant results. The platinum foil was cleaned in nitric acid or nitric and chromic acids after sealing up in the reaction bulb, and in the manometric experiments as many experiments as possible were completed without removal from the apparatus. In the sealed-tube experiments, the platinum was washed with nitric acid after each experiment. For the experiments at 80° and 120° the inside wall of a bulb was platinised by evaporating on it a solution of platinum chloride in alcohol and igniting. This formed a very active platinum mirror, which, however, did not adhere to the glass well enough for quantitative work.

After many trials with different forms of silver catalyst for the manometric experiments, silver mirrors were deposited on the inner surface of the reaction bulbs by reducing ammoniacal silver nitrate with sugar solution. This surface was active, but usually disintegrated and became inactive after one or two experiments. For the sealed-bulb experiments, silver powder was prepared by reducing silver solution with formaldehyde, drying and igniting the product, and thoroughly mixing. Weighed amounts of this catalyst were used, each portion being used only once.

*Experiments with Platinum Catalyst.*

Evidence that the reaction yielding carbon dioxide is the only one occurring to any great extent on platinum is given by the following experiments with sealed bulbs.

Expt.	Catalyst.	Temp.	Ratio CO/H <sub>2</sub> .
1.	Platinised bulb	78°	0.034
2.	" "	118	0.025
3.	Foil 1	184	< 0.01
4.	"	209	< 0.01

Sabatier and Mailhe have classed platinum among the catalysts which bring about the decomposition of formic acid into carbon dioxide and hydrogen. From the results of Hinshelwood, Hartley, and Topley, glass could be placed among these at higher temperatures, but not at lower temperatures. The present results show that the behaviour of platinum in this respect is not analogous to that of glass, since the reaction yielding carbon monoxide never predominates.

The platinum foil used catalysed the formation of carbon dioxide and hydrogen from carbon monoxide and water only very slightly at 235°; even at 260°, an active foil converted only one-half the original amount of carbon monoxide into carbon dioxide in seventy hours.

The reaction appears to be unimolecular, the velocity coefficient usually remaining constant to within about 10 per cent. in a given experiment.

Temperature 206°.

$t$ (minutes).	$p$ (mm.).	$k = 1/t \log_{10} \frac{p_{\infty}}{p_{\infty} - p}$
4.0	126	0.0275
6.3	186	0.0274
9.1	246	0.0272
13.3	316	0.0262
20.9	406	0.0265
32.2	486	0.0270
End point	563 $p_{\infty}$	---

In some cases, however, a marked increase is observed during the experiment, which may be due to a catalytic action of the reaction products, but is more plausibly to be attributed to changes in the activity of the surface. An accelerating influence is difficult to explain, on the basis of adsorption, in the same way as "poisoning."

The most striking variations were shown, however, in successive experiments, the velocity changing by as much as 100 per cent., although nothing had been done to the catalyst beyond cooling, admitting air, and boiling off a fresh charge of formic acid. The

fluctuations showed both increases and decreases, with at first a general tendency to increase. These made the main object, which was to determine the temperature coefficient of the velocity, very difficult to achieve. In the first experiments made, a "poisoning" effect appeared, which was at first attributed to carbon monoxide. It was not observed later and remains unexplained.

(a) *Manometric Experiments*.—Attempts to get the temperature coefficient from consecutive experiments proving unsatisfactory, it was decided to deduce the coefficient from a single experiment as follows. The reaction was allowed to proceed at the lower temperature until about half complete. The apparatus was then transferred to the bath at the higher temperature, and data taken starting from a new  $t_0$  and  $p_0$ . After the end-point at the higher temperature had been obtained, the apparatus was returned to the lower temperature, and the end-point there determined; the gas-law afforded a check on the readings. The constants were now calculated for each 100 mm. of rise in  $p$  by the formula

$$k = \frac{1}{t_2 - t_1} \cdot \log_{10} \frac{p_\infty - p_1}{p_\infty - p_2}$$

and the last value of  $k$  in the first part of the experiment compared with the first value in the second part. A summary of the results follows.

	Temp.	$k$ (average).	$k$ (initial).	$k$ (final).	Ratio for 10° rise.
1. (a)	141°	0.00175	0.00165	0.00180	
(b)	209	0.100	0.090	0.100	1.77
2. (a)	141	0.00140	0.00160	0.00140	
(b)	209	0.0700	0.0680	0.0760	1.77
3. (a)	141	0.00160	0.00160	0.00165	
(b)	209	0.0540	0.0525	0.0570	1.67
4. (a)	141	0.00235	0.00230	0.00310	
(b)	209	0.0635	0.0650	0.0640	1.57
5. (a)	141	0.00180	—	0.0030	
(b)	209	0.260	0.23	0.30	1.89
6. (a)	141	0.00300	0.00260	0.00310	
(b)	210	0.083	0.073	0.098	1.70
				Average	1.73

Averaging all the values of  $k$  at different temperatures obtained from eleven other experiments and plotting  $\log k$  against temperature, a value of 1.70 for the temperature coefficient was obtained.

(b) *Sealed-bulb Experiments*.—The great difficulty of the manometric experiments lay in the variability of the catalytic surface. This was to some extent overcome by the device of the broken experiment just described; but the comparative simplicity of the sealed-bulb experiments rendered another method possible, namely,

to carry out a large number of experiments and treat the results from a statistical point of view. This was justifiable, since the variation in the activity of the platinum through the series was quite random, and apparently depended only on the extent to which the surface, even after cleaning with nitric acid, remained contaminated with minute amounts of foreign matter. It is now recognised that films of molecular thickness may enormously influence the catalytic activity.

Eight experiments were made at each of four temperatures. The mean of the eight results for each temperature, together with the "probable error," which measures the extent of the random variations, is given below. It must be emphasised that these variations have nothing to do with the experimental errors of the single experiments, which were negligible in comparison with the variations due to changes in the surface.

Temp.	139.5°	181.8°	205.5°	234°
$k \times 10^4$	$3.9 \pm 2.3$	$53.5 \pm 13$	$150 \pm 29$	$617 \pm 190$

Plotting  $\log k$  against temperature, the temperature coefficient from the slope is found to be 1.76 with a probable error of about 0.1. Thus both this series and the manometric experiments show that the decomposition on platinum into hydrogen and carbon dioxide has a high temperature coefficient, which is of the same order as, but rather less than, that of the corresponding reaction on glass.

#### *Experiments with Silver Catalyst.*

*Manometric Experiments.*—A long series of experiments was made both in the manometric apparatus and in sealed bulbs with silver foil as catalyst. The foil showed some activity, but it was of the same order as that of the glass walls of the bulb.

Eventually the catalyst was deposited as a mirror on the bulb as described above. Recourse was had to the "broken experiment" to obtain consistent results from which the temperature coefficient could be calculated. Analysis showed a small amount of carbon monoxide, but probably not more than could be accounted for by the reaction on the glass.

Expt.	Bulb.	Temp.	$k$ .	Ratio for 10° rise.	Ratio CO CO <sub>2</sub>
1 (a)	6	184°	0.0012		
(b)	6	222	0.014	1.91	0.06
2 (a)	7	177	0.0024		
(b)	7	250	0.25	1.89	—
3 (a)	7	184	0.0036	1.90	—
(b)	7	218	0.033	1.92	0.06

—  
Average 1.91

With regard to the secondary interaction of carbon monoxide and water, a silvered bulb, such as was used in the manometric experiments, heated for fifteen hours at 250–260°, showed no trace of the formation of carbon dioxide. In a test with the reduced-silver powder used in the sealed-bulb experiments, heating for twenty hours at 250° gave only 3 per cent. of carbon dioxide.

*Sealed-bulb Experiments with Reduced Silver.*—The catalyst used in each case was 1 gram of silver powder prepared as described. The results obtained at the two temperatures used are tabulated below.

Expt.	Fraction decomposed.	$k_{\text{total}} \times 10^4$ .	$\frac{\text{CO}}{\text{H}_2}$ Temperature 184.6°.	$k_{\text{CO}_2} \times 10^5$ .
1	0.091	0.063	0.339	0.047
2	0.093	0.140	0.597	0.088
3	0.094	0.150	0.690	0.089
4	0.151	0.070	0.230	0.057
5	0.247	0.128	0.352	0.095
6	0.251	0.137	0.233	0.111
7	0.450	0.184	0.155	0.159
8	0.548	0.194	0.243	0.159
Average	0.241	0.133	—	0.100
Temperature 141.4°.				
9	0.114	0.0021	0.826	0.0011
10	0.118	0.0037	0.933	0.0019
11	0.180	0.0020	1.320	0.0008
12	0.194	0.0040	0.350	0.0030
13	0.578	0.0064	0.050 (?)	0.0061
Average	0.237	0.0037	—	0.00264

From the average value of the widely divergent values of  $k$  at the two temperatures the temperature coefficient for 10° rise over this range is 2.32.

$k$  shows a general tendency to increase with time (that is, with the fraction decomposed). At present we are not able to state whether this is due to an influence of the products or to changes in the activity of the catalyst, which becomes activated during the reaction. The point is under investigation.

The larger part of the acid decomposes into carbon dioxide and hydrogen on the silver; the reaction on glass gives only insignificant amounts of carbon dioxide at these temperatures. But it was found both by extrapolation and by direct experiment that the reaction on glass could account for a large proportion, perhaps all, of the carbon monoxide formed at 141.4°. For this reason values of  $k_{\text{CO}}$  are not given. At 184.6°, the reaction on glass could account for only about one-seventh of the total carbon monoxide, so that we may conclude that  $k_{\text{CO}}$  for silver has a temperature



coefficient considerably higher than  $k_{\text{Co}}$  for glass. The value for the temperature coefficient of  $k_{\text{CO}_2}$  is calculated from values which seem to increase with the fraction decomposed, but since the average value of this fraction is the same for both temperatures, any error due to this will be minimised.

*Summary of Temperature Coefficients for  $k_{\text{CO}_2}$ .*

	Ratio for 10°.	Range.	Heat of activation from formula $\frac{d \log k}{dT} = Q/RT^2$
Platinum	1.73	141—209°	21,800 cal.
	1.70	141—209°	21,100 „
	1.76	141—234°	23,800 „
		Mean	22,200 „
Silver	1.91	184—250°	30,800 cal.
	2.32	141—184°	31,700 „
		Mean	31,300 „
Compare glass	—	—	28,000 „

It may be noticed that the platinum, which is the most efficient catalyst, is in this case associated with the lowest heat of activation, with respect to one and the same mode of reaction, namely, decomposition into carbon dioxide and hydrogen.

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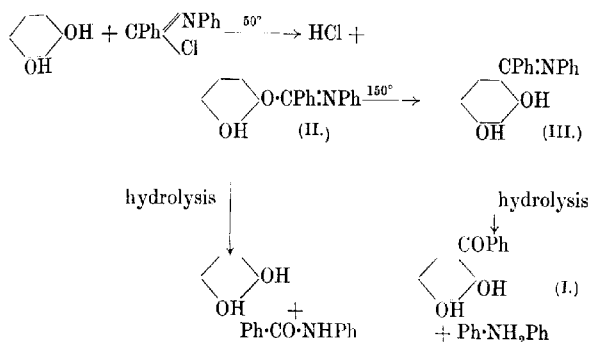
[Received, July 4th, 1922.]

*CC.—Imino-aryl Ethers. Part I. N-Phenylbenz-imino-m-hydroxyphenyl Ether and the Synthesis of 2:4-Dihydroxybenzophenone.*

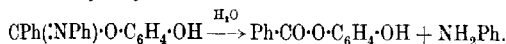
By ARTHUR WILLIAM CHAPMAN.

IN connexion with syntheses of aromatic ketones which were being performed by Hoesch's method (*Ber.*, 1915, 48, 1122), the author's attention was directed to some observations by Stephen (T., 1920, 117, 1529) relating to this type of reaction. This worker found

that benzoylresorcinol (I) resulted from the hydrolysis of the product of interaction of benzanilideiminochloride and resorcinol, first at 50° and then for a short time at 150°. In explanation, it was suggested that the first stage of the reaction consisted in the formation of *N*-phenylbenzimino-*m*-hydroxyphenyl ether (II), which at the higher temperature underwent isomerisation to the anil of benzoylresorcinol (III):



In support of this view, it was stated that the primary condensation product, on hydrolysis by dilute hydrochloric acid, yielded benzanilide and resorcinol. It seems more probable, however, that the imino-ether (II) would furnish aniline and *m*-hydroxyphenyl benzoate on hydrolysis:



This conjecture was strengthened by reference to the literature (Pinner, "Die Imidoaether," 1892; Hantzsch, *Ber.*, 1893, **26**, 926; Lander, T., 1901, **79**, 690; 1902, **81**, 591; 1903, **83**, 320, 766), and therefore it was decided to attempt the isolation of the imino-ether in question, and to investigate its behaviour under the various conditions employed in Stephen's condensation.

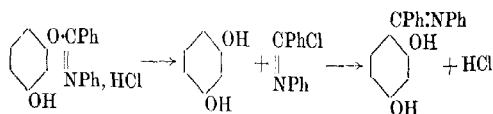
After several unsuccessful attempts, a suitable method for the preparation of the imino-ether was devised as an adaptation of the methods of Hantzsch and Lander (*loc. cit.*), and consisting in the addition of an ethereal solution of benzanilideiminochloride to a solution of a large excess of resorcinol in absolute alcohol containing slightly more than the theoretical amount of sodium ethoxide.

As had been anticipated, the imino-ether prepared in this way was converted by hydrolysis with hydrochloric acid into *m*-hydroxy-

phenyl benzoate and aniline, the identity of the former product being established by comparison with a sample prepared by the action of benzoyl chloride on resorcinol (Einhorn and Hollandt, *Annalen*, 1898, **301**, 104). The formation of benzanilide and resorcinol observed by Stephen on hydrolysis of the product obtained by heating a mixture of benzanilideiminochloride and resorcinol at 50°, would therefore appear to indicate that the materials were to a very large extent unchanged by the treatment. A repetition of his experiment confirmed this conclusion, since hydrogen chloride, the other product of the reaction, was evolved only in very small amount.

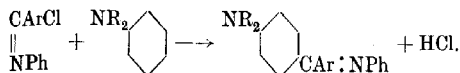
Furthermore, the imino-ether underwent no apparent change when heated for half an hour at 155–160°, but at 170° or above, darkening occurred accompanied by some depression of melting point. In the latter case, hydrolysis of the product yielded, in addition to benzoic acid, a small proportion (1·8 per cent.) of benzanilide, but no benzoylresorcinol, and a similar result was obtained at 185–195°. It followed, therefore, that the imino-ether itself was not responsible for the formation of the anil of benzoylresorcinol as stated by Stephen. A repetition of his experiment confirmed the formation of benzoylresorcinol, and an examination was accordingly made of the behaviour of another possible intermediate product, namely, the imino-ether hydrochloride. This compound was easily prepared by passing dry hydrogen chloride into a solution of the imino-ether in benzene; and when heated at 150–160° for fifteen minutes and subsequently hydrolysed with hydrochloric acid, it furnished a 4·5 per cent. yield of benzoylresorcinol. By heating at 165–175° for twenty-five minutes, the yield was increased to 20 per cent.

This indicates that it is the imino-ether hydrochloride rather than the imino-ether itself from which the anil of benzoylresorcinol can be produced on heating; and therefore it would seem very probable that the reaction in question depends on preliminary dissociation of the hydrochloride into resorcinol and benzanilideiminochloride, followed by a process of direct substitution:



It has long been known that the anils of di-*N*-substituted amino-benzophenones may be prepared by the action of *N*-arylarylimino-

chlorides on tertiary aromatic amin (Meister, Lucius, & Brüning, 1887, D.R.-P. 41,751, 44,077); for example,



In the present instance, it has been found that benzoylresorcinol can be prepared from the product of interaction of benzanilideimino-chloride and resorcinol at 100°, at which temperature the imino-ether hydrochloride undergoes no change. It seems difficult, therefore, to escape the conclusion that in this case, and hence in the experiment described by Stephen, direct substitution takes place, and that this represents the normal course of keto-anil formation.

It will be noted that these experiments form a further contribution to the evidence which is gradually accumulating to show that, at least in some cases, the so-called "indirect substitution" (Blanksma, *Rec. trav. chim.*, 1902, **21**, 281; 1904, **23**, 202), involving the migration of a substituent from the side-chain into the nucleus of an aromatic compound, in reality depends on a preliminary fission by hydrolysis or other analogous reaction, followed by a process of direct substitution. Thus Orton and Jones showed that the production of *C*-chloroacetanilides from *N*-chloroacetanilides in the presence of hydrochloric acid proceeds by a preliminary formation of acetanilide and chlorine, the latter then directly attacking the nucleus (T., 1909, **95**, 1456). Similarly, it has recently been shown that dimethylaniline hydrochloride accompanies *o*- and *p*-toluidine hydrochlorides in the product of heating methylaniline hydrochloride; and therefore methyl chloride is a product of the reaction and probably responsible for the toluidine formation (Beckmann and Correns, *Ber.*, 1922, **55**, [B], 852).

Further experiments on the thermal decomposition of imino-aryl ethers and their hydrochlorides, which have shown that these reactions differ markedly from those of the imino-alkyl ethers, will be dealt with in a future communication.

#### EXPERIMENTAL.

*N*-Phenylbenziminom-*m*-hydroxyphenyl Ether.—Sodium (6 grams) and resorcinol (7.5 grams) were dissolved in absolute alcohol (250 c.c.), a stream of hydrogen being passed through the flask throughout the process. The resulting solution was at once treated with an ethereal solution of benzanilideiminochloride prepared from benzanilide (50 grams) and phosphorus pentachloride (Wallach, *Annalen*, 1877, **184**, 77), when sodium chloride was immediately

precipitated. After twelve hours, the ether and most of the alcohol were distilled off, and the residue poured into water, the oil obtained rapidly solidifying. By crystallisation from alcohol, 42 grams of material (57 per cent. calculated on the weight of benzanilide) were obtained; the melting point, 164—165°, was raised to 167—168° by repeated crystallisation.

*N*-Phenylbenzimidino-*m*-hydroxyphenyl ether forms very pale yellow, microscopic prisms, and is moderately soluble in alcohol, sparingly soluble, in hot or cold benzene or in ether, very sparingly soluble in light petroleum, and almost insoluble in water (Found: N = 5.03.  $C_{19}H_{15}O_2N$  requires N = 4.84 per cent.).

The hydrochloride, prepared from hydrogen chloride and the imino-ether (15 grams) in hot benzene (600 c.c.), was precipitated as a very pale yellow, crystalline powder (11.8 grams), and dried in a vacuum over sulphuric acid and solid sodium hydroxide. When quite fresh, it melts at 178—179° with decomposition to a red liquid. For analysis, it was repeatedly treated with small quantities of hot water containing nitric acid; the hydrochloric acid was estimated in the combined filtrates (Found: HCl = 11.0.  $C_{19}H_{15}O_2N \cdot HCl$  requires HCl = 11.2 per cent.).

*Hydrolysis of N*-Phenylbenzimidino-*m*-hydroxyphenyl Ether.—The imino-ether (2 grams) was heated for five minutes with concentrated hydrochloric acid (7 c.c.) in a boiling water-bath, an equal bulk of water added, and the heating continued for five minutes. By crystallising the solidified oil from dilute alcohol, scales (0.65 gram), m. p. 130—131°, were obtained, with a smaller quantity of less pure material. By repeated crystallisation from a mixture of chloroform and light petroleum, the melting point was raised to 133—134°, and this was not depressed by admixture with *m*-hydroxyphenyl benzoate (m. p. 133—134°) prepared by Einhorn and Hollandt's method (*loc. cit.*). The presence of anilino in the acid liquor from the hydrolysis was demonstrated by the usual qualitative tests.

*Behaviour of N*-Phenylbenzimidino-*m*-hydroxyphenyl Ether when Heated.—Neither the appearance nor the melting point of the imino-ether was changed when a sample was heated for thirty minutes in an oil-bath at 155—160°. The imino-ether (10 grams) was then heated for thirty-five minutes at 170°, fusion being complete in twenty minutes. The dark brown product softened below 120°, but melted at 163—165°. The hydrolysis with repeatedly renewed quantities of hydrochloric acid (Stephen, *loc. cit.*) was considerably facilitated in the presence of glass-wool, on which the oily material distributed itself. The substance crystallising

from the cooled filtered solutions was separated by sodium carbonate, in which benzoylresorcinol is soluble, into a soluble and an insoluble portion. The sodium carbonate solution furnished, on acidification, pure benzoic acid only (1.6 grams), which melted at 122—123°. The insoluble portion (0.13 gram) was identified as benzanilide.

A similar experiment, in which 7 grams of the imino-ether were heated at 185—195° for thirty minutes, gave 0.86 gram of benzoic acid and 0.09 gram of benzanilide, m. p. 163°.

*Behaviour of N-Phenylbenziminom-m-hydroxyphenyl Ether Hydrochloride when Heated.*—The heating and the hydrolysis were conducted in the same way as in the case of the imino-ether, 4 grams of material being employed. One experiment was performed at 150—160° for fifteen minutes, slight fusion being observed at the bottom of the tube; whilst another, at 165—175° for twenty-five minutes, resulted in fusion to a dark brown mass with slight evolution of hydrogen chloride. The material separating from the cooled filtered solutions was repeatedly extracted with hot benzene. By evaporation of the extracts and crystallisation of the residues from water, pale brown, slender prisms were obtained, m. p. 144—145°, which were identified as benzoylresorcinol by comparison with a sample prepared by the Hoesch reaction. The respective yields at 150—160° and 165—175° were 0.11 gram (4.5 per cent.) and 0.5 gram (20 per cent.). The small residue insoluble in benzene was shown to be the hydrochloride of diphenylbenzenylamidine by conversion into the base (m. p. 146—147°) and by direct comparison with a sample of diphenylbenzenylamidine prepared by the action of benzanilideiminochloride on aniline.

When the hydrochloride (2.3 grams) was heated in a boiling water-bath for thirty-five minutes, its melting point and appearance underwent no change.

In order to imitate as far as possible the conditions employed in the fusion of benzanilideiminochloride and resorcinol, the hydrochloride was mixed with benzanilide (0.5 gram) and resorcinol (0.5 gram) and again heated in the water-bath for thirty-five minutes. The mass partly fused and a trace of hydrogen chloride was evolved. The residue was then hydrolysed as before, but the sole product was pure benzoic acid, m. p. 122—123°.

*Condensation of Benzanilideiminochloride and Resorcinol at 100°.*

—An intimate mixture of resorcinol (2 grams) and benzanilideiminochloride (3.9 grams, b. p. 210—211°/46 mm.) was heated in a boiling water-bath for twenty minutes. The fused mass separated into two layers, the lower being much darker and more viscous than the upper, and a little hydrogen chloride was evolved. The residue was hydrolysed by warm dilute hydrochloric acid (50 c.c.) and the

product separated by crystallisation, first from dilute alcohol, and then from a mixture of chloroform and light petroleum, into pure benzanilide (1.3 grams, m. p. 162.5—163°) and benzoyl-resorcinol (0.7 gram, m. p. 143—144°). From the mother-liquors a very small quantity of material, m. p. 112—115°, probably impure *m*-hydroxyphenyl benzoate, was obtained.

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### CCl.—Crystalline Glucose-ammonia and isoGlucosamine.

By ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI.

IN 1893, Lobry de Bruyn and Franchimont (*Rec. trav. chim.*, 1893, **12**, 286) obtained a crystalline derivative of glucose by dissolving ordinary dextrose in ammoniacal methyl alcohol. They found that the same substance is obtained by treating the two isomeric pentaacetyl glucoses with alcoholic ammonia. They state that this substance is isomeric with the glucosamine obtained by the hydrolysis of chitin.

When the compound is boiled with an excess of *N*/10-sulphuric acid for some time, it is hydrolysed, and the above-named authors point out that the nitrogen can in this way be estimated by titration.

In this paper it is also stated that lactose and galactose give crystalline derivatives when treated with ammoniacal methyl alcohol. Fructose is said to give an amorphous and a crystalline derivative.

The aqueous solution of the lactose derivative is said to give off ammonia after a time, and Lobry de Bruyn and Franchimont remark, "*La lactosamine est à ce qu'il semble une aldehyde-ammoniaque.*" This evolution of ammonia, as we shall show, is also true of the glucose derivative (see p. 1686).

Stone (*Amer. Chem. J.*, 1895, **17**, 191) obtained a crystalline substance by suspending dextrose in absolute ethyl alcohol which had been saturated with ammonia. It was easily soluble in water, reduced Fehling's solution somewhat more strongly than dextrose, melted at 122–123°, and had a specific rotatory power of  $[\alpha]_D^{22}$  22.7°, without exhibiting mutarotation. Distilled with sodium hydroxide, the whole of the nitrogen was found to be evolved as ammonia. A titration gave 8.74 per cent. of ammonia. The

author accordingly believed the substance to be an ammonia derivative,  $C_6H_{12}O_6 \cdot NH_3$ , analogous to aldehyde-ammonia.

There seemed little doubt that the substance obtained by Stone was identical with that obtained by Lobry de Bruyn and Franchimont, and this was assumed in further papers by Lobry de Bruyn (*Rec. trav. chim.*, 1895, **24**, 98; *Ber.*, 1895, **28**, 3082).

In the last two papers, Lobry de Bruyn, in referring to Stone's method of analysis—distilling with sodium hydroxide—suggests that under these conditions the whole of the ammonia is not evolved. He recrystallised the substance, as obtained by his method, from 95 per cent. methyl alcohol and then found it to melt with decomposition and darkening at  $127-128^\circ$ . A complete elementary analysis showed that it had the composition of a glucosamine,  $C_6H_{13}O_5N$ , and the author remarks (*Rec. trav. chim.*, 1895, *loc. cit.*) "*La d-glucosamine n'est pas par conséquent un aldehyde-ammoniaque; elle est isomère avec la chitosamine (encore nommée à tort glucosamine) et avec l'isoglucosamine et l'acrosamine de M. Fischer, qui cependant jusqu'ici n'ont été obtenues que sous forme de sirops ou de sels.*"

Lobry de Bruyn (*Ber.*, 1895, *loc. cit.*) describes a number of similar derivatives of other sugars. He suggests that the glucose

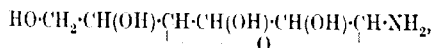
NH  
derivative contains the grouping  $CH-CH \cdot OH$ .

In von Lippmann's "*Chemie der Zuckerarten*" (1904, vol. I, p. 504), it is stated that Wohl has suggested that the grouping

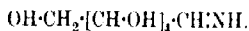
NH  
— $CH \cdot (CH \cdot OH)_2 \cdot CH \cdot OH$  is the more probable; but no reference is given to an original paper by Wohl.

Irvine, Thomson, and Garrett (T., 1913, **103**, 238) have examined the products of the action of ammonia and alkylamines on glucose and fructose.

Discussing the probable constitution of Lobry de Bruyn's "glucosamine," they reject the formulæ of Lobry de Bruyn and of Wohl as being inconsistent with their observations that ammonia is without action on alcoholic solutions of saccharose and of  $\alpha$ -methylglucoside. They state that although all the results obtained are not entirely consistent, the bulk of the evidence points to the formula



or to the imino-formula,



Whilst recognising that either of these two formulæ might result from the dehydration of a derivative of the aldehyde-ammonia type, they assert that there is no positive evidence of the formation

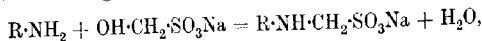
of such an additive compound from glucose, Stone's results (*loc. cit.*) having been called in question by Lobry de Bruyn.

There can be no doubt that the crystalline compound obtained by Lobry de Bruyn, when purified by recrystallisation from methyl alcohol, has the elementary composition assigned to it by that chemist. At the same time, the possibility is not excluded that the initial product of the action of ammonia on glucose in methyl-alcoholic solution is a glucose-ammonia and that by recrystallisation from methyl alcohol it loses one molecule of water. Our own work on the action of ammonia in aqueous solution on dextrose (*J. Soc. Chem. Ind.*, 1922, **41**, 151r) renders this highly probable. We have indeed direct evidence in confirmation of this view. The product first obtained by Lobry de Bruyn's method melts, as stated by Stone, at  $122-123^{\circ}$ , thus several degrees lower than the melting point of the recrystallised product ( $127-128^{\circ}$ ). It contains the percentage of nitrogen required by glucose-ammonia. In aqueous solution, it reduces Fehling's solution, ammoniacal silver nitrate, and solutions of salts of other heavy metals, giving metallic mirrors just as does the glucose-ammonia recently described by us (*loc. cit.*). Like glucose-ammonia, the aqueous solution of Lobry de Bruyn's substance decomposes, when heated, with the evolution of carbon dioxide and the production of dark-coloured products (*ibid.*).

From these considerations it would seem to be established that the product formed by the action of ammonia on dextrose in methyl alcoholic solution is the same as in aqueous solution, namely, glucose-ammonia. In the latter case, however, isodynamic changes occur (compare Ling and Nanji, *loc. cit.*). The theoretical importance of the problem is, however, so great that we deemed it necessary to furnish still further evidence.

Since aldehyde-ammonia compounds are capable of being reduced to primary amines, thus  $R\cdot CHO, NH_3 \rightarrow R\cdot CH(OH)\cdot NH_2 + H_2 = R\cdot CH_2\cdot NH_2 + H_2O$ , glucose-ammonia should yield on reduction the glucamine of Maquenne and Roux (*Compt. rend.*, 1901, **132**, 980), thus  $OH\cdot CH_2\cdot [CH\cdot OH]_4\cdot CH(OH)\cdot NH_2 + H_2 = OH\cdot CH_2\cdot [CH\cdot OH]_4\cdot CH_2\cdot NH_2 + H_2O$ , and this we find to be the case.

Finally, Knoevenagel and Mercklin (*Ber.*, 1904, **37**, 4087) having shown that formaldehyde sodium bisulphite condenses with compounds containing the amino-group, thus :



we have succeeded in condensing the supposed glucose-ammonia with formaldehyde sodium bisulphite with the production of the  $\omega$ -sodium sulphonate,  $OH\cdot CH_2\cdot [CH\cdot OH]_4\cdot CH(OH)\cdot NH\cdot CH_2\cdot SO_3Na$ .

We contend, therefore, in the light of the evidence furnished, that we have definitely proved that the crystalline compound obtained by the action of ammonia on dextrose in methyl-alcoholic solution is glucose-ammonia, whilst for the constitution of the anhydride, isoglucosamine, we can at present add nothing to the deductions put forward by Irvine, Thomson, and Garrett (*loc. cit.*).

#### EXPERIMENTAL.

##### *Preparation of Glucose-Ammonia.*

Instead of dissolving dextrose in ammoniacal methyl alcohol, the method adopted by Lobry de Bruyn and Franchimont, we found the following mode of procedure a more convenient one.

A current of ammonia (generated by warming concentrated aqueous ammonia, *d* 0.880, and scrubbing the gas through a tower of quicklime) is passed into a suspension of dextrose (25 grams) in 95 per cent. methyl alcohol (200 c.c.). The dextrose dissolves after a time and a further 25 grams are added. This is repeated until 250 grams in all of dextrose have been dissolved. Care should be taken not to allow the temperature to rise above 20–30°. After a while, crystals separate in small rosettes. Separation commences at room temperature in about a fortnight, but this may be greatly expedited by cooling in an ice-chest, and scratching the sides of the flask with a rod. In these circumstances the syrupy solution solidifies to a solid magma of crystals in less than a fortnight. The crystals are collected and the solvent is removed as completely as possible by suction. Examination under the microscope shows that the substance is homogeneous. It is, however, hygroscopic and cannot be dried over sulphuric acid, since under these conditions it at first loses some ammonia and then one molecule of water. It was found possible, however, to dry small portions on a porous plate. The dry substance then melted at 123–124° with decomposition and darkening. Stone (*loc. cit.*) gives the melting point as 122–123°. Its specific rotatory power in aqueous solution was found to be  $[\alpha]_D^{20} + 20.3^\circ$  (*c* = 5). Heated with phenylhydrazine acetate in the ordinary manner, it gives phenylglucosazone. It reduces Fehling's solution, ammoniacal silver nitrate solution, and solutions of salts of other heavy metals giving metallic mirrors, and when its aqueous solution is boiled ammonia is given off and the solution darkens.

It is thus seen that the substance behaves similarly to the glucose-ammonia recently described by us (*loc. cit.*). The nitrogen content by the ordinary Kjeldahl method was found to be N = 6.86, whilst by the micro-Kjeldahl method (Ling and Price, *J. Soc. Chem. Ind.*,

1922, **41**, 149r) it was found to be  $N = 6.83$ . (Glucose-ammonia,  $C_6H_{15}O_6N$ , requires  $N = 7.10$ . Glucosamine,  $C_6H_{13}O_5N$ , requires  $N = 7.93$  per cent.)

Analysis therefore confirms the view that the substance is glucose-ammonia. As will be seen, however, the results are low, this being due partly to the absorption of moisture during the weighing-out of the portion for analysis, and partly to the loss of ammonia which occurs.

The product obtained as above described may be recrystallised from 95 per cent. methyl alcohol as stated by Lobry de Bruyn (*loc. cit.*). The crystals thus obtained are in the form of needles and melt at  $127-128^\circ$  (*ibid.*).

Analysis showed that they had the composition of a glucosamine as stated by Lobry de Bruyn, thus  $N = 7.5$  to  $7.44$  per cent. These values, it will be seen, are intermediate between those required for glucose-ammonia and glucosamine, this being possibly due to incomplete dehydration.

#### *Production of Glucamine.*

It is evident that the reduction of a compound of the nature of glucose-ammonia must be conducted in neutral solution. Three methods were tried, (1) catalytic hydrogenation, (2) reduction with aluminium amalgam, and (3) electrolytic reduction. Of these, No. 3 was found to be the most efficient and No. 1 the least.

No. 1.—Following Mignonac (*Compt. rend.*, 1921, **172**, 223), the unpurified glucose-ammonia was dissolved in absolute methyl alcohol so as to make an approximately 10 per cent. solution, and the catalyst (finely divided metallic nickel, specially prepared by electrolytic reduction) was introduced, oxygen being carefully excluded. A current of hydrogen was now passed through at the ordinary temperature. The reaction is at an end when no more hydrogen is absorbed. At this point, the catalyst is filtered off and the solution dealt with by appropriate methods.

No. 2.—For the reduction with aluminium amalgam, the unpurified glucose-ammonia (10 grams) was dissolved in 100 c.c. of 95 per cent. methyl alcohol and treated with 2.5 grams of aluminium amalgam prepared as follows: Aluminium turnings\* are first freed from oil by boiling with an aqueous solution of sodium hydroxide until a copious evolution of hydrogen has set in. The metal is then rinsed with water and allowed to act on a 0.5 per cent. solution of mercuric chloride for one to two minutes. The amalgam is finally washed with alcohol and ether. The reduction is carried

\* We are indebted to Dr. R. Seligman for supplying us with aluminium turnings.

out at a temperature of  $40^{\circ}$ , and when the reaction is complete the aluminium hydroxide is filtered off. The filtrate contains the base together with other products, for example, mannitol.

No. 3.—For the electrolytic reduction, an approximately 10 per cent. solution of the glucose-ammonia in 95 per cent. methyl alcohol serving as the cathodic liquid was introduced into a thin porous pot. A saturated solution of sodium carbonate was used as the anodic liquid. The electrodes used were of lead. The current density was 0.2 ampere per sq. cm. and the *E.M.F.* 6–7 volts. The temperature rises slowly during the reduction, but under the given conditions keeps constant at about  $40^{\circ}$ . The passage of the current is continued for about four hours. This method was found to be the most satisfactory of the three.

The solutions obtained by the three reduction methods all gave the characteristic tests for glucamine as described by Maquenne and Roux. With nitrous acid, nitrogen was evolved; they showed strongly alkaline reactions, dissolved ferric hydroxide giving a reddish-brown solution, and cupric hydroxide giving a dark blue solution. With mercuric chloride and with silver nitrate, precipitates were formed, which after a time, or more quickly when heated, changed to dark, metallic deposits. When heated with iodine solution, substances were formed possessing the odour of iodoform. Finally, unlike the parent glucose-ammonia, they formed salts. Glucamine was, in fact, isolated as the oxalate, which separated out in characteristic, hexagonal plates (Maquenne and Roux, *loc. cit.*). We deemed it unnecessary to make an analysis.

The condensation product of glucose-ammonia with formaldehyde sodium bisulphite was prepared as follows: Ordinary 40 per cent. formalin (7.5 c.c.) is mixed with a solution of sodium hydrogen sulphite (10.4 grams) in water (20 c.c.), and the mixture is kept at  $70^{\circ}$  for about half an hour, when the odour of formaldehyde will have disappeared. Glucose-ammonia (20 grams) is then dissolved in the solution, and the mixture kept in an incubator at  $38$ – $40^{\circ}$  for two days. To isolate the salts, advantage was taken of the fact that the *m*-sodium sulphonate derivatives are only sparingly soluble in alcohol. The solution is transferred to a separating funnel and an equal volume of 80 per cent. alcohol added, when the condensation product is precipitated as a syrupy liquid. The mixture is well shaken to remove the unaltered reagents, the syrup removed from the alcoholic layer, and again shaken with four successive quantities of 80 per cent. alcohol of about the same volume as the syrup. Finally, the syrup is separated and run into a Petri dish, which is placed in a vacuum desiccator over concentrated sulphuric acid, and, after a time, it sets to a hard, amorphous, almost colourless

mass which is extremely hygroscopic (Found: Na = 7.16, 7.18.  
 $C_7H_{16}O_9NSNa$  requires Na = 7.34 per cent.).

In conclusion, we have to express our thanks to Mr. Leslie Warren for the assistance he has rendered us during the prosecution of this work.

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### CCII.—Limits for the Propagation of Flame at Various Temperatures in Mixtures of Ammonia with Air and Oxygen.

By ALBERT GREVILLE WHITE.

OF recent years a fair amount of work has been carried out on the oxidation of ammonia by means of oxygen and atmospheric air, the general method being to pass a preheated mixture of the gases over a catalyst maintained at a high temperature. Manufacturing experience showed that under certain conditions an ammonia-air mixture burst into flame near the catalyst, the flame travelling back to the preheater. This led to the determination of the limits for the propagation of flame in air and oxygen mixtures of ammonia up to the highest temperatures likely to be attained by preheating.

According to Lunge ("Coal Tar and Ammonia," London, 1916, Part III, p. 1304), ammonia burns only with great difficulty in atmospheric air, requiring constant heating. Henry (*Ann. Phil.*, 1825, 25, 424) states that mixtures of air and ammonia are not explosive, but that by the continuous action of electric sparks they are slowly burnt. Schlumberger and Piotrowski, on the other hand (*J. Gasbeleucht.*, 1914, 57, 941) found that mixtures of 16.5 per cent. to 26.8 per cent. by volume of ammonia in air explode in vessels of the form chosen by them. In a Bunte burette there was no explosion, but gradual combustion from about 19 per cent. to 25 per cent. Ammonia-oxygen mixtures are known to be explosive, the limits for the propagation of flame being given by Reis (*Z. physikal. Chem.*, 1914, 88, 513) as below 1.5 per cent. and above 80 per cent. of ammonia by volume.

#### EXPERIMENTAL.

The ammonia used was procured from a large gas cylinder. After use for some little time, three careful analyses showed that it contained 1.0 per cent. of moisture and 0.4 per cent. of nitrogen.

The moisture was estimated by prolonged agitation over sticks of sodium hydroxide, the ammonia being afterwards absorbed in concentrated sulphuric acid to estimate the residual gas. The presence of hydrogen could not be detected.

Most of the determinations were carried out in glass tubes 5 cm. in internal diameter, but similar tubes 7.5 cm. in diameter were also used at room temperature. All the tubes were 1.5 m. long from shoulder to shoulder and were provided with stopcocks of 6 mm. bore at one end and a ground glass cap about 9 mm. in diameter at the other. The cap was used instead of a stopcock to enable the tube to be pushed into the furnace readily. Limit trials were always made with both ends of the tube closed. The gas mixture was ignited by means of 1 to 2 mg. of guncotton yarn fired by means of an induction coil spark produced at a removable glass-insulated brass wire electrode. The electrode was introduced just before firing, the joint being made air-tight with plasticine. Electrodes had to be renewed frequently owing to corrosion of the inside brass wire by ammonia. Tubes were always carefully dried before use, usually by blowing air dried by calcium chloride through the tube, which had been washed with acetone.

Above room temperature, determinations were carried out inside an electric furnace which could be rotated round a horizontal axis perpendicular to that of the furnace. The furnace was 1.4 m. long and was supplied with a heavy iron furnace-tube 7.5 cm. in diameter, which projected slightly at the ends. The maximum temperature variation along the tube under the conditions obtaining during an experiment was less than  $20^{\circ}$ , if we neglect the 15 cm. at each end. The temperature of the gas at the middle of the furnace was indicated by means of a fine copper-constantan thermocouple, which was removed immediately before firing. The couple was connected with a potentiometer apparatus which indicated a change of temperature of  $1^{\circ}$  readily. The glass thermocouple sheath provided an exit for excess ammonia-air at lower temperatures, and as it was 90 cm. long and of 2 mm. internal diameter, it was impossible for atmospheric air to diffuse back into the mixture.

The mixtures used were made up by volume. The measuring vessels consisted of three elongated glass tubes of 200, 250, and 600 c.c. capacity, respectively, to each of which a 50 c.c. burette was sealed. These could be calibrated by weighing full of water. The whole of each vessel was water-jacketed, the water being air-stirred.

It was found absolutely necessary to boil all the mercury used at least every second day. If this were not done, the moisture picked up by the mercury absorbed ammonia. When this happened in



the measuring vessel, as the latter was finally connected with an evacuated tube or bottle, more than the calculated amount of ammonia was used. The error from this source could become serious. Thus, in one preliminary experiment, a tube supposed to contain 19.0 per cent. of ammonia was found on analysis to contain 19.6 per cent. Taking adequate precautions, however, the method gave accurate results. It was often tested by analysis, when the calculated and experimental figures generally agreed to less than 0.5 per cent. of the ammonia used. The gases were mixed by shaking with a few c.c. of small beads for twenty minutes.

For lower limit determinations below  $350^{\circ}$ , and upper limit determinations below  $250^{\circ}$ , the gas mixture required was made up in the limit tube. This tube was then inserted into the furnace, which was kept  $20^{\circ}$  to  $30^{\circ}$  above the temperature required, and the mixture was fired as soon as it reached that temperature. The tube and its contents were generally seven to eight minutes in the furnace before firing.

It was found that at  $350^{\circ}$  and  $250^{\circ}$  for the lower and upper limits respectively, this time was sufficient to affect the result obtained very appreciably, owing to preliminary oxidation of ammonia. A fresh method was accordingly adopted at and above these temperatures. The tube was kept in the furnace at the required temperature, whilst the mixture was made up in a 15-litre glass bottle. The tube was then evacuated to a pressure of less than 2 mm. of mercury by means of a Gaede box pump, and the necessary amount of mercury run into the bottle containing the ammonia-air mixture. By turning a 2-way cock the tube could be filled with ammonia-air from the bottle and was then ready for firing in about half a minute. The amount of mercury introduced into the bottle always displaced more than sufficient mixture to fill the tube, the excess being allowed to escape past the firing cap. The differences between results obtained by the two methods seemed to depend on the direction of propagation, particularly for the upper limit. For this limit the results obtained at  $450^{\circ}$  for upward, horizontal, and downward propagation by the first method were 31.2, 29.6, and 31.6 per cent., respectively, those for the second method being 33.9, 33.1, and 32.0 per cent.

Ammonia-oxygen mixtures were made up in much the same way as when air was used, except that after evacuation with a Gaede pump the tubes were first filled with oxygen from a cylinder. The only impurity present in this gas in appreciable quantity was nitrogen, of which it contained less than 1 per cent. After partial evacuation, the ammonia was introduced in the usual way and the tube filled to atmospheric pressure with oxygen. At the upper

limit, the results were confirmed satisfactorily by measuring in the oxygen and making up to atmospheric pressure with ammonia.

Throughout the work the accuracy aimed at was 1 per cent. on the ammonia present. The results represent the percentage of ammonia introduced into a given volume of the mixture, the ammonia being taken to be 98.6 per cent. of the volume of crude ammonia added. No attempt was made to correct for the slightly increased percentage of nitrogen in the "atmosphere" used.

As test experiments showed that varying the moisture content of a tube from 0.4 to 2.5 per cent. did not appear to affect the limit obtained to the accuracy required, ordinary undried air was used for making up the mixtures.

#### Results.

The results obtained are shown in Table I, all being expressed as percentage by volume.

TABLE I.

*Showing the ranges throughout which ammonia-air and ammonia-oxygen mixtures propagate flame at various temperatures.*

Mixture.	Tube.	Temp.	Upwards.	Horizontal.	Downwards.
Ammonia air .....	5	18°	16.1—26.6	18.2—25.5	None
	"	60	—	—	None
	"	70	—	—	22.1—23.3
	"	90	—	—	21.0—24.6
	"	140	15.0—28.7	17.0—27.5	19.9—26.3
	"	250	14.0—30.4	15.9—29.6	17.8—28.2
	"	350	13.0—32.2	14.7—31.1	16.0—30.0
	"	450	12.3—33.9	13.5—33.1	14.4—32.0
Ammonia oxygen ...	7.5	18	17.1—26.4	17.4—26.3	None
	5	18	15.3—79	16.7—79	18.1—79
	"	250	—	14.8—	15.8—
	"	450	—	12.6—	13.5—
	7.5	18	14.8—	15.6—	17.3—

The flame, particularly in ammonia-air mixtures, was often of a vivid yellow colour. Great care had to be taken in determining the upper limit for mixtures with oxygen, as using slightly too little ammonia was apt to cause a violent explosion.

The limits with air determined in 7.5 cm. tubes are interesting, the ones for upward being almost the same as those for horizontal propagation. The corresponding pairs of limits as determined in a 5 cm. tube differ appreciably. We thus find that for upward propagation the limits are narrower for the wider tube than for the other, though the reverse holds for the limits for horizontal propagation. The latter result is the one to be expected, both on the

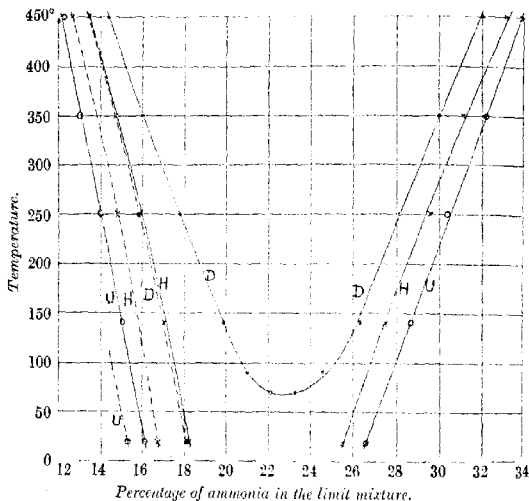
grounds of convection effect and as the result of wall cooling. The anomalous result obtained for upward propagation seems to be due to the instability of the flame in the wider tube, as in this case the flame in trials below the limit found appeared to be jerked out.

The best idea of the results is probably to be obtained from Fig. 1, in which the limits obtained in 5 cm. tubes at various temperatures are indicated. This shows that no flame is propagated downwards in ammonia-air mixtures until the original temperature

FIG. 1.

*Showing the limits for the propagation of flame in ammonia-air and ammonia-oxygen mixtures.*

*Air limits shown by full, oxygen limits by dotted, lines.*



of the mixture approaches 70°. The optimum mixture for flame propagation downwards would appear to contain about 22.5 per cent. of ammonia. The mixture for perfect combustion contains just under 22 per cent. Up to 140°, the range for propagation downwards increases very rapidly, but above this point the upper limit increases at much the same rate as for propagation in the other directions. This is not the case for the lower limit, which decreases a good deal more rapidly for downward propagation than for propagation upwards or horizontally. For the latter the lower limit seems to decrease by about 7 per cent. per 100°, whilst the

downward limit above  $140^{\circ}$  seems to decrease by about 10 per cent. for the same rise in temperature.

Owing to the large amount of inert matter in its molecule, ammonia could scarcely be expected to give limit results strictly comparable with those of ordinary combustible gases. This factor, entailing the presence of such a large amount of ammonia at the lower limit, presumably explains why the lower-limit results for oxygen are so definitely lower than those determined for mixtures containing air. Terres (*J. Gasbeleucht.*, 1920, **63**, 785, 805, 820, 836), using such substances as carbon monoxide, hydrogen, benzene, and methane, found the lower limit little affected by the substitution of oxygen for air. The variation of the lower limits in oxygen with temperature is very similar to that of the lower limits in air for upward and horizontal propagation.

A comparison of the results for ammonia-air mixtures with those obtained for vapour-air mixtures (this vol., p. 1244) is interesting. In ammonia mixtures, once above the temperature at which propagation downwards begins to fail, the limits for propagation upwards and downwards do not differ much, even for the upper limit. This behaviour differs from that of vapours at the upper limit, when the ratio of the two values normally varies from 1.3 to 1.7. As a result of this the upper and lower limits for ammonia at any one temperature are nearly symmetrically situated about the mixture for complete combustion for all directions of propagation. The corresponding rule for vapours holds only for downward propagation. The accuracy with which the rule holds for ammonia may be gauged by an examination of Fig. 1, or from the fact that the sum of the limits for each of the eighteen pairs determined lies from 42.7 to 46.6, twice the value of the mixture for perfect combustion being just under 44.

An attempt to calculate the lower limit for horizontal propagation in the case of ammonia gives 15.7 per cent., if we use a constant 1120 and take its net calorific value as 73.5. The value found for ammonia-air is 17.4 per cent. and that for ammonia-oxygen 15.6 per cent. The other relationships found for vapour limits are only true for ammonia in the neighbourhood of  $500^{\circ}$ .

Calculation shows that the theoretical temperature of combustion found for ammonia at the lower limit is a good deal higher than that of any of the vapours examined. The results of calculation for both limits are shown in Table II, specific heats (at constant pressure) extrapolated from those of Holborn and Henning (*Ann. Physique*, 1905, [iv], **18**, 739; 1907, [iv], **23**, 809) being used for nitrogen, carbon dioxide, and steam. The molecular values for oxygen and nitrogen are assumed to be equal, and the values for

ammonia taken are those given by Lewis and Randall (*J. Amer. Chem. Soc.*, 1912, **34**, 1128). No correction has been made for loss of heat.

TABLE II.

*Showing the theoretical temperature of combustion attained by horizontal limit mixtures of ammonia in air and downward limit mixtures in oxygen. Tube 5 cm. in diameter.*

Temp. of original mixture.	Lower limit in air.		Lower limit in oxygen.		Upper limit in air.	
	% ammonia in limit mixture.	Flame temp.	% ammonia in limit mixture.	Flame temp.	% ammonia in limit mixture.	Flame temp.
20°	18.2	1630°	18.1	1620°	25.5	1760°
150	16.9	1620			27.7	1770
250	15.9	1620	15.8	1610	29.6	1790
350	14.7	1610			31.1	1820
450	13.5	1620	13.5	1620	33.1	1840

Confining our attention to the lower limits, it will be seen that to ensure propagation, the flame temperature has to be much the same, whether the mixture is originally at 20° or 450°. This makes untenable the idea that the effective ignition temperature functioning during the propagation is that normally determined. An explanation covering the facts is afforded if we consider the effective ignition temperature to approximate closely to that of the flame. It is just possible, of course, that the equality of temperature of flame found may be due to the compensating effect of different factors. Thus, the ignition temperature which functions might conceivably increase in the correct proportion as the mixture became more dilute. There is no evidence of any such phenomenon, however, and it is exceedingly unlikely that any such effect should occur. Dixon and Crofts (*T.*, 1914, **105**, 2036) found that the ignition temperatures of mixtures of hydrogen and oxygen decreased under similar conditions. Conclusions of a similar general nature can be drawn from the upper-limit results, although the agreement is not nearly so good, and the flame temperature differs considerably from that found for the lower limit.

An examination of the effect of temperature on the limits for the propagation of flame in methane-air mixtures has been made by Wheeler and Mason (*T.*, 1918, **113**, 45). The theoretical temperatures of the flames in some of the limit mixtures determined by them are given below:

Original temperature .....	20°	200°	400°	600°	700°
Lower limit .....	6.0	5.05	4.00	3.35	3.25
Calculated temperature of flame	1470°	1410°	1360°	1400°	1460°

The flame temperatures do not vary much, and it seems, as has been suggested by Taffanel and Le Floch (*Compt. rend.*, 1913, **157**,

595), that a certain definite intensity of reaction is necessary for propagation. The rule will probably be found to be fairly general. Further experiments on these lines are now proceeding.

I desire to express my thanks to Messrs. Nobel Industries, Ltd., and particularly to Mr. Rintoul, Manager of the Research Section, for facilities accorded for the carrying out of this work.

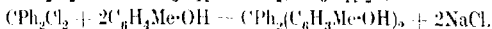
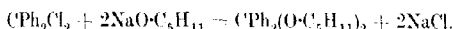
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ARDEER.

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### CCIII.—*The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride. Part III.*

By JOHN EDWIN MACKENZIE.

IN former publications by the author and his collaborators (T., 1896, **69**, 985; 1901, **79**, 1204; 1904, **85**, 790; Clough, T., 1906, **89**, 771; P., 1910, **26**, 170), the production of a number of ketals of the type  $C(Ph_2(OMe)_2)$  and of hydroxy-compounds of the type  $C(Ph_2(C_6H_4-OH)_2)$  is described. The preparation of diisooamyloxydiphenylmethane and of dihydroxy-*m*- and dihydroxy-*p*-tolyl-diphenylmethanes has now been carried out and forms the subject of the present paper. The reactions may be represented thus :



In the table given below, it is interesting to note the influence of different groups and of different arrangements of the same group on the melting and boiling points of these substances. Thus the substitution of an ethoxy- for a methoxy-group produces a lowering of the melting point which is of the same order as that exhibited by the corresponding substituted *l*-malic and *d*-tartaric acids :

	M. p.
(1) $HO_2C-CH_2-CH(OMe)-CO_2H$ .....	89°
(2) $HO_2C-CH_2-CH(OEt)-CO_2H$ .....	76
(3) $HO_2C-CH(OMe)-CH(OMe)-CO_2H$ .....	151
(4) $HO_2C-CH(OEt)-CH(OEt)-CO_2H$ .....	126

On the other hand, when a hydrogen atom in a benzene nucleus is replaced by a methyl group, the melting point is lowered, as will be seen on comparing the melting points of the corresponding dimethoxydiphenylmethane and dimethoxyphenyl-*p*-tolylmethane and of the corresponding dihydroxytetraphenylmethane and dihydroxy-*m*- and dihydroxy-*p*-tolyl-diphenylmethanes.

The boiling point, as is usual, rises with the increase in the number of carbon atoms in the molecule.

Name and formula.	M. p.	B. p.
Dimethoxydiphenylmethane, $(C_6H_5)_2C(O-CH_3)_2$ ...	106°	288°
Diethoxydiphenylmethane, $(C_6H_5)_2C(O-C_2H_5)_2$ ...	52°	294°
Dipropoxydiphenylmethane, $(C_6H_5)_2C(O-C_3H_7)_2$ ...	33°	204°/40 mm.
Di <i>iso</i> amloxydiphenylmethane, $(C_6H_5)_2C(O-C_8H_{11})_2$ Oil		190–200°/15 mm.
Dibenzyloxydiphenylmethane, $(C_6H_5)_2C(O-CH_2-C_6H_5)_2$	104°	305°/40 mm.
Di- <i>β</i> -naphthoxydiphenylmethane, $(C_6H_5)_2C(O-C_{10}H_7)_2$ .....	137°	—
Dimethoxyphenyl- <i>p</i> -tolylmethane, $C_6H_5Me-CPh(O-CH_3)_2$ .....	Oil	163°/15 mm. 186°/26 mm. 312°/80 mm.
Dihydroxytetraphenylmethane, $(C_6H_5)_4C(C_6H_4OH)_2$ .....	284°	—
Dihydroxy- <i>m</i> -tolylidiphenylmethane, $(C_6H_5)_2C(C_6H_4Me-OH)_2$ .....	234°	—
Dihydroxy- <i>p</i> -tolylidiphenylmethane, $(C_6H_5)_2C(C_6H_4Me-OH)_2$ .....	126°	—
Di- <i>α</i> -hydroxynaphthylidiphenylmethane, $(C_6H_5)_2C(C_{10}H_6OH)_2$ .....	209°	—
Benzylidene dimethyl ether, $C_6H_5CH(O-CH_3)_2$ ...	—	194°
Benzylidene diethyl ether, $C_6H_5CH(O-C_2H_5)_2$ ...	—	222°
Dihydroxytriphenylmethane, $C_6H_5CH(C_6H_4OH)_2$	160°	—

## EXPERIMENTAL.

*Diisoamloxydiphenylmethane*.—2.75 Grams of sodium were dissolved in 54 grams of *iso*amyl alcohol (b. p. 130–130.5°), heated in an oil bath at 170°. To the cold, jelly-like solution were added 14.3 grams of benzophenone chloride. No reaction took place at room temperature, but on heating at 130° a vigorous action set in, and after heating at 170° for eighteen hours the supernatant solution was neutral. The ethereal solution of the product was separated from the sodium chloride, the ether removed, and the residual liquid distilled at 25 mm. pressure, the fraction coming over between 220° and 225° weighing 15 grams. This colourless oil, even after redistillation at 190–200/15 mm., could not be obtained crystalline, a hard glass being formed in liquid air. The oil had  $d$  0.981, and was readily miscible with chloroform, ethyl acetate, light petroleum, or benzene, but only to a small extent with methyl or ethyl alcohol (Found: C = 80.98, 80.87; H = 9.52, 9.42.  $C_{23}H_{32}O_2$  requires C = 81.17; H = 9.41 per cent.).

This compound appears to be very stable in a dry atmosphere. In a vacuum desiccator over concentrated sulphuric acid, it lost 7.4 per cent. in two hundred and one days, the theoretical loss for the splitting off of *iso*amyl ether being 46.4 per cent. In this respect it differs very materially from the corresponding methoxy-, ethoxy-, and *isobutoxy*-derivatives, each of which dissociates into benzophenone and the corresponding ether.

In a previous communication (T., 1904, 85, 791), mention was made of the production of benzhydrol in the above described preparation. Benzhydrol has also been isolated in an attempt to prepare diisopropoxydiphenylmethane, the product melting at 66–67° (Found: C = 84.55; H = 6.95. Calc., C = 84.78; H = 6.52 per cent.).

*Attempt to prepare Di-tert.-amylxydiphenylmethane.*—4.6 Grams of sodium were added to a mixture of 20 grams of *tert.*-amyl alcohol and 50 grams of xylene, the mixture being boiled until all the sodium had dissolved. On the addition of 24.1 grams of benzophenone chloride, the solid sodium amyl oxide dissolved, and after ten minutes vigorous ebullition took place. The mixture was heated at the b. p. for twelve hours, and the liquid then showed a neutral reaction. After the addition of ether, removal of the precipitated sodium chloride, and of the ether, the residual brown liquid was heated at 60°/50 mm. The residue in the distilling flask deposited a brownish-yellow solid on cooling. This was partly decolorised by boiling its solution in benzene with animal charcoal and subsequently washing the light brown crystals obtained from this solution with small quantities of acetone. From the product, a colourless distillate was obtained at above 300°/35 mm., which solidified after some time. After crystallisation from a mixture of chloroform and alcohol, the crystals melted at 220–221° (Found: C = 92.13; H = 6.15.  $C_{26}H_{20}$  requires C = 93.97; H = 6.03 per cent.). Repeated analyses gave the percentage of hydrogen between 5.95 and 6.15, but the percentage of carbon was always decidedly low—between 91.5 and 92.13. These results pointed to the product being tetraphenylethylene, m. p. 221° (Biltz, *Annalen*, 1897, 296, 231). To confirm this supposition, 1.0096 grams were dissolved in 30 c.c. of carbon tetrachloride and brominated in sunlight by the addition of a solution of bromine in this solvent. The colour did not disappear at once on the addition of the bromine solution, indicating that the bromine derivative formed was a substitution, and not an additive, product. After removing the excess of bromine by a current of dry air and the solvent by evaporation, the residue weighed 2.0610 grams, the theoretical weight for  $C_{26}H_{16}Br_4$  being 1.971 grams. It was redissolved in carbon tetrachloride and the colour removed by animal charcoal. The crystals obtained from carbon tetrachloride and alcohol were recrystallised from glacial acetic acid and dried in a desiccator over solid caustic potash. They then melted at 242–243° (Biltz, *loc. cit.*, gives 248–249°) (Found: Br = 50.25 per cent.). The product is therefore undoubtedly tetra-*p*-bromotetraphenylethylene.

*Dibenzoxydiphenylmethane.*—To the description of this substance



previously given (T., 1896, 69, 993) may be added the observation that when kept at a temperature of  $220^{\circ}$  for some time it dissociates into benzophenone and dibenzyl ether, the latter vaporising and condensing as a colourless liquid. The former, when seeded with a crystal of benzophenone, became crystalline and after drying on a porous tile melted at  $48-49^{\circ}$ .

*Dihydroxytetraphenylmethane.*—An experiment in which 18.8 grams of phenol and 23.7 grams of benzophenone chloride were heated at  $135-155^{\circ}$  for twenty-five hours gave the theoretical loss in weight (7.3 grams) and a nearly quantitative yield of dihydroxytetraphenylmethane (compare T., 1901, 79, 1210).

*Dihydroxy-m-tolyldiphenylmethane.*—*m*-Cresol (2 mols.) and benzophenone chloride (1 mol.) were mixed in a round-bottomed flask provided with a ground-in condenser tube terminated by a calcium chloride tube. Both these substances are viscid liquids and they do not mix freely with each other, so that occasional stirring was resorted to in order to increase the surface contact between them. Heating at  $120^{\circ}$  did not appear to hasten the evolution of hydrogen chloride, and even at the end of six weeks, during which the mixture was heated daily at the above temperature and under a pressure of 30 mm., gas was still being evolved. The dark red, gummy condensation product, which was very readily soluble in the ordinary organic solvents other than light petroleum, was dissolved in benzene and nearly decolorised by repeatedly boiling with fresh quantities of animal charcoal. After removing the benzene, the gummy residue was triturated with small quantities of light petroleum to remove the gum and then crystallised from warm light petroleum. The colourless crystals melted at  $234^{\circ}$  and were readily soluble in the ordinary organic solvents with the exception of light petroleum (Found: C = 84.94, 84.98; H = 6.47, 6.50.  $C_{27}H_{24}O_2$  requires C = 85.22; H = 6.36 per cent.).

*Dihydroxy-p-tolyldiphenylmethane.*—To 9 grams of *p*-cresol were added drop by drop 19 grams of benzophenone chloride. A vigorous reaction took place with evolution of copious fumes of hydrogen chloride. The mixture was shaken frequently, and after three days it had set to a black solid, from which the occluded hydrogen chloride was removed by evacuation in a desiccator containing solid caustic potash. The solid was readily soluble in benzene, alcohol, or ether, but with difficulty in light petroleum. By repeatedly digesting its solution in benzene with fresh quantities of animal charcoal and removing the benzene, a nearly colourless product composed of crystals embedded in resinous matter was obtained. This product, which became dark green on exposure to the air, was triturated with small quantities of light petroleum

and then crystallised from a mixture of this solvent with ether. The colourless crystals melted sharply at  $126^{\circ}$  (Found: C = 85.45, 85.50; H = 6.69, 6.58.  $C_{27}H_{24}O_2$  requires C = 85.22; H = 6.36 per cent.).

The author desires to thank Mr. A. F. MacCulloch, M.A., B.Sc., for assistance in carrying out the preparation of the dihydroxy-tolyldiphenylmethanes.

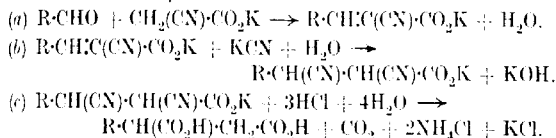
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#### CCIV.—*Syntheses of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. Part I. Acids containing Aromatic Residues.*

By ARTHUR LAPWORTH and JOHN ALEXANDER McRAE.

DURING the course of investigations on the addition of hydrogen cyanide to unsaturated compounds it was found by one of us (P., 1904, 20, 245) that hydrogen cyanide readily forms additive compounds with alkylidenecyanoacetic acids forming products of the type  $R\cdot CH(CN)\cdot CH(CN)\cdot CO_2H$ , from which, on hydrolysis, alkylsuccinic acids could be prepared. The reactions involved were the following:



The process did not differ in general principle from that employed by Bredt and Kallen (*Annalen*, 1896, 293, 350), who used (malonic) esters instead of the free acids, but has a great advantage in economy, as ethyl malonate is replaced by the inexpensive potassium cyanoacetate solution, which is made as required by mixing solutions of potassium chloroacetate and potassium cyanide under definite conditions (compare also this vol., p. 49 *et seq.*).

The authors now find that the process gives excellent results in certain instances, although it is not so generally applicable as the very convenient process discovered by Higson and Thorpe (T., 1906, 89, 1455). These workers start, however, from the costly ethyl cyanoacetate, the latter in the form of its sodium derivative being allowed to react with the cyanohydrins of aldehydes and ketones in

alcoholic solution. The present authors are of opinion that the superiority of this process is probably to be traced to the fact that unsaturated esters always react with cyanides much more readily than do the corresponding acids (compare this vol., p. 50).

The results of a more detailed examination which is in progress on the synthesis of  $\alpha$ -substituted succinic acids are most readily dealt with in separate sections, and the present communication has reference solely to cases where aldehydes containing aromatic nuclei or unsaturated aliphatic residues were the starting points.

(A).—*Preparation and Properties of Alkylidenecyanoacetic Acids.*

Benzaldehyde, piperonal, anisaldehyde, and cinnamaldehyde give good yields of the corresponding alkylidenecyanoacetic acids when brought in contact with solutions of potassium (or sodium) cyanoacetate. The use of pure cyanoacetate (Strebel, D.R.P. 108355; Haarmann and Reimer, *ibid.*, 189252; Tiemann, *Ber.*, 1898, **31**, 3325) seems quite unnecessary. Lapworth (P., 1904, **20**, 245), in his syntheses of substituted succinic acids, used crude potassium cyanoacetate made from chloroacetic acid, and later, Clarke and Francis (*Ber.*, 1911, **44**, 273) made the intermediate alkylidenecyanoacetic acids from potassium cyanoacetate prepared from the more expensive bromoacetic acid. When the crude cyanoacetates are used, however, it is desirable to employ conditions such as are described in the experimental section, otherwise the products are liable to be contaminated with unchanged aldehyde and possibly also other impurities, and the yields of purified compound are poor.

(1) *Preparation of  $\alpha$ -Cyano- $\beta$ -phenylacrylic Acid from Benzaldehyde and Crude Sodium Cyanoacetate.*—(a) A concentrated neutral solution of mixed sodium and potassium cyanoacetate was made from monochloroacetic acid and potassium cyanide by the method described by Phelps and Tillotson (*Amer. J. Sci.*, 1908, [iv], **26**, 267).

To such a solution, made from 50 grams of monochloroacetic acid, and occupying (after neutralisation, if necessary) about 200 c.c., there are added 45 grams of freshly distilled benzaldehyde and 20 c.c. of 20 per cent. aqueous sodium hydroxide. On shaking, the reaction sets in rapidly, the temperature rises to about 50°, and the contents of the flask become semi-solid. After an hour, hydrochloric acid is added in slight excess and the separated cyanophenylacrylic acid, mixed with some sodium chloride, is collected and washed with water, thoroughly dried in the air, and washed with a little cold benzene. (This washing with benzene is necessary, as for some reason which, in spite of many experiments on the subject, has not been satisfactorily accounted for, benzaldehyde is invariably present

in the crude product and, unless eliminated, renders subsequent purification difficult and attended with a fall in yield.) The crude washed product, allowing for the content of sodium chloride, amounts to 80–90 per cent. of that theoretically possible and affords the pure acid without difficulty on recrystallisation from hot water, dilute alcohol, or hot benzene. The acid has the properties ascribed to it by Fiquet (*Ann. Chim. Phys.*, 1893, [vi], 29, 433).

(b) The following process was suggested by Knoevenagel's observations on the application of amines in allied condensations, but is novel inasmuch as the catalyst is applied in aqueous solution.

To the solution of crude sodium potassium cyanoacetate made as indicated above there are added enough hydrochloric acid to liberate about half the cyanoacetic acid present and then 18.6 grams of aniline hydrochloride, 25 c.c. of alcohol, and 48 grams of benzaldehyde, and the whole is shaken continuously; condensation proceeds in the cold and after the lapse of fifteen to twenty minutes cyanophenylacrylic acid begins to separate. Agitation must now be very vigorous for five minutes to prevent localisation of the benzaldehyde, and then the whole may be set aside for half an hour. Excess of hydrochloric acid may now be added, the precipitated cyanophenylacrylic acid collected by filtration, washed, and purified as above. The yield of crude product of 90–95 per cent. purity is 85–90 per cent. of that theoretically obtainable from the quantity of benzaldehyde used.

(2) *Preparation of  $\alpha$ -Cyano- $\beta$ -piperonylacrylic Acid.*—(a) Piperonal (26.3 grams; 0.18 mol.) was added to sodium-potassium cyanide solution (150 c.c.) made from 25 grams (0.25 mol.) of monochloroacetic acid and containing 20 c.c. of 20 per cent. sodium hydroxide and 20 c.c. of alcohol. On shaking vigorously, the mixture quickly becomes semi-solid owing to separation of sodium cyanopiperonylacrylate. The mixture, on acidification, gave cyanopiperonylacrylic acid, which was collected, washed with water, and, after air-drying, washed with benzene to remove unchanged piperonal. After two recrystallisations from alcohol, the acid melted at 228°; Bechert (*J. pr. Chem.*, 1894, [ii], 50, 19), who made it by hydrolysis of its ethyl ester, gives the melting point as 230°. The yield of crude acid, calculated on the weight of piperonal used, was 95 per cent. of the theoretical quantity.

(b) To a solution of 300 c.c. of potassium sodium cyanoacetate made from 50 grams (0.5 mol.) of monochloroacetic acid are added 20 c.c. of hydrochloric acid (*d* 1.16), 18.9 grams of aniline hydrochloride, 67.5 grams (0.45 mol.) of piperonal, and 50 c.c. of alcohol. A yellow colour develops at once, showing that action has begun, and on warming at 35–40° the solution begins to deposit cyano-

piperonylacrylic acid. On shaking vigorously for five minutes, the mixture presents the appearance of a semi-solid, yellow, crystalline mass. Excess of hydrochloric acid is added, and the precipitated cyanopiperonylacrylic acid is collected and purified as described above. The yield of material, after washing with benzene, is 85–90 per cent. of the theoretical quantity calculated on the weight of piperonal used, and the product is pure enough for conversion into the hydrogen cyanide additive compound.

(3) *Preparation of  $\alpha$ -Cyano- $\beta$ -anisylacrylic Acid.*—Anisaldehyde (27.2 grams; 0.20 mol.) was added to sodium-potassium cyanoacetate solution made from 25 grams (0.25 mol.) of monochloroacetic acid and containing 20 c.c. of 20 per cent. sodium hydroxide and 20 c.c. of alcohol. On shaking, the mixture quickly became semi-solid. Cyanoanisylacrylic acid is obtained by adding hydrochloric acid in excess. The crude acid is collected and purified as described for cyanopiperonylacrylic acid. The yield, calculated on the weight of anisaldehyde used, is 80–85 per cent. of the theoretical. After two recrystallisations from alcohol, the acid melted at 226° and had the properties ascribed to it by Bechert (*J. pr. Chem.*, 1894, [ii], 50, 11).

(4) *Preparation of  $\alpha$ -Cyano- $\beta$ -styrylacrylic Acid.*—It is not advantageous in the preparation of this compound to use aniline hydrochloride as a catalyst, as a very large proportion of neutral product is then formed. The synthesis is readily carried out, however, by means of sodium hydroxide much as described for cyanophenylacrylic acid. The product has the properties ascribed to it by Fiquet (*Ann. Chim. Phys.*, 1893, [vi], 29, 433; compare also Rinkes, *Rec. trav. chim.*, 1920, 39, 200).

(B).—*Properties of  $\alpha$ -Cyano- $\beta$ -arylacrylic Acids.*

During the course of this work, a few reactions of the cyanoarylacrylic acids have been noted which are worthy of mention.

When  $\alpha$ -cyano- $\beta$ -phenylacrylic acid is warmed with resorcinol and concentrated sulphuric acid at 150–200° for a few minutes, the mixture then cooled, treated with excess of sodium hydroxide, and poured into water, a pronounced green fluorescence is observed, which, however, is not nearly so intense as when phenylsuccinic acid is used.

The cyano-group of cyanophenylacrylic acid is very resistant to hydrolysis by acids and remains unaffected when the substance is dissolved in concentrated sulphuric acid or fuming hydrochloric acid.

The additive compounds of the cyanoarylacrylic acids are interesting. The acids dissolve fairly freely in strong sodium

hydrogen sulphite solution, and this must be due to addition at the ethylenic linking with formation of salts of the type  $X\cdot CH(SO_3Na)\cdot CH(CN)\cdot CO_2Na$ , for, at the concentrations used, the free alkylidenecyanoacetic acids and their sodium salts are only partly dissolved by water. Unlike most of the hydrogen sulphite additive products obtained by Knoevenagel and Lange (*Ber.*, 1904, **37**, 4059, 4069) from aliphatic alkylidenemalonate esters, these compounds are capable of reconversion into their constituents; for example, if the solution of cyanophenylacrylic acid in sodium hydrogen sulphite solution is made alkaline with excess of sodium hydroxide, the sodium salt of cyanophenylacrylic acid is precipitated; again, if that solution is rendered only slightly alkaline so that no sodium salt is precipitated, addition of hydrochloric acid then results in the deposition of cyanophenylacrylic acid. Owing to such properties of these additive compounds it is possible to prepare cyanophenylacrylic acid in satisfactory yield by bringing together benzaldehyde sodium hydrogen sulphite, and sodium cyanoacetate in presence of sufficient alkali to decompose the former compound.

As cyanopiperonylacrylic acid is yellow and its sodium salt colourless and sparingly soluble, whilst their additive products with sodium hydrogen sulphite are usually much more soluble, the conditions under which additive compounds are formed and dissociated respectively are very readily traced; this acid reacts less rapidly both with bisulphite and with potassium cyanide than does cyanophenylacrylic acid, but much more rapidly than does cyanostyrylacrylic acid. The possibilities of exchange of the elements of sodium hydrogen sulphite for those of hydrogen cyanide have not yet been fully explored.

Cyanophenylacrylic acid appears to form very readily an additive compound, probably  $C_6H_5\cdot CH(NH_2)\cdot CH(CN)\cdot CO_2H$ , with ammonia, as it dissolves very freely in aqueous ammonia and is not reprecipitated on addition of excess of mineral acid. If, on the other hand, this ammoniacal solution is made strongly alkaline with excess of sodium hydroxide, sodium cyanophenylacrylate separates in the solid form and then, for the first time, the subsequent addition of mineral acid precipitates cyanophenylacrylic acid. Similar reactions are noted with cyanopiperonylacrylic acid.

(C).—*Addition of the Elements of Hydrogen Cyanide to Alkylidenecyanoacetic Acids containing Aromatic Nuclei.*

This addition takes place in presence of a considerable excess of potassium cyanide, and in agreement with the kinetic measurements made by W. J. Jones (*T.*, 1914, **105**, 1547), it was found that

the unsaturated acid made from piperonal reacts much more slowly than does that from benzaldehyde, the process being rendered still more troublesome by the sparing solubilities of the salts of the acid; under suitable conditions, however, and especially if the ammonium salt of the unsaturated acid is used, good yields of the required products are obtained. Cyanostyrylacrylic acid, in similar circumstances, did not appear to react, and this was quite in accordance with the low additive capacity of ethyl cinnamylidenemalonate (Thiele and Meisenheimer, *Annalen*, 1899, 306, 247).

The properties of the dicyano-acids which represent the initial products of this additive process are not attractive, and the acids were not isolated as such, especially as it was found more satisfactory to effect partial or complete hydrolysis of these products as in the next step.

Details of the modes in which conversion of the products into substituted succinic acids may be effected are given in the following sections, where there will also be found descriptions of the various products obtained during the course of the work.

(1) *Addition of Hydrogen Cyanide to  $\alpha$ -Cyano- $\beta$ -phenylacrylic Acid, and Preparation of Phenylsuccinic Acid.*—(a) Finely powdered cyanophenylacrylic acid (17.3 grams), suspended in 160 c.c. or more of water, is dissolved by the very gradual addition of 10 per cent. sodium hydroxide solution. The acid goes into solution slowly, but it is not advisable to attempt to hasten the process by warming on account of the sensitiveness of the acid to hot alkali. To this neutral solution of sodium phenylacrylate there is added a solution made by mixing potassium cyanide (20.9 grams) in water (60 c.c.) with acetic acid (10.4 grams) in water (20 c.c.). A precipitate of sodium (or potassium) cyanophenylacrylate usually appears at first, but ultimately dissolves and after twenty-four hours the reaction is complete.

The conversion of the additive product into phenylsuccinic acid may be effected in a variety of ways, of which the following gave the best results.

The solution obtained as above is treated with hydrochloric acid until it is nearly but not quite acid towards Congo-red, and the resulting turbidity is removed by repeated filtration. The clear liquid is now mixed with a large excess of hydrochloric acid, and a rapid current of air is then passed through it. An oil makes its appearance, but this soon begins to deposit crystals and ultimately solidifies. After about forty-eight hours' continuous aspiration, no further deposition takes place, and the material may be collected; in quantity, it approaches 85 per cent. of that theoretically possible.

Agitation of the solution by means of a mechanical stirrer did

not lead to the same satisfactory results as were obtained by the aspiration process described.

The crude crystalline product \* is covered with ten times its weight of hydrochloric acid saturated at 0°. The whole is placed in the ice-chest over-night, then warmed gently on the sand-bath until the greater part of the excess dissolved gas is expelled, and finally heated more vigorously until the evolution of carbon dioxide ceases and the liquid boils with bumping. The solution is then diluted to about 250 c.c., boiled for a short time with the addition of animal charcoal, and filtered; on cooling, pure phenylsuccinic acid crystallises out and a small further quantity is obtained by evaporating the mother-liquor to half its volume. The yield is almost quantitative. The over-all yield calculated from the weight of benzaldehyde used is about 65–70 per cent. of the theoretical. The identity of the acid was established, after a second recrystallisation by its melting point (167°) and by titration with *N*/10-sodium hydroxide (Found: equiv. = 97. A dibasic acid,  $C_{10}H_{10}O_4$ , requires equiv. = 97).†

\* This product appears to be a mixture of two or more compounds which have not been separated owing to the difficulty experienced in finding a suitable solvent for recrystallisation. It dissolved readily in hot water, acetic acid, and in hot methyl alcohol, but did not separate from the resulting solutions until most of the solvent had evaporated. It was nearly insoluble in petroleum or benzene.

A sample prepared by extracting the crude crystalline material with hot amyl alcohol presented under the microscope the appearance of a homogeneous material consisting of prismatic needles and it melted and decomposed sharply at 180° (Found: C = 60.4; H = 4.6; N = 14.4 per cent. Equivalent = 218). These numbers indicate conversion of one -CN group in the dicyano-acid which is the first additive product into CO-NH<sub>2</sub>, and the substance is probably mainly the acid,  $CHPh(CO \cdot NH_2) \cdot CH(CN) \cdot CO_2H$  (Calc., C = 60.6; H = 4.6; N = 12.9 per cent. Equivalent = 218), but perhaps, judging by the high number for nitrogen, contaminated with some of the unaltered dicyano-acid,  $CHPh(CN) \cdot CH(CN) \cdot CO_2H$ . The compound readily lost carbon dioxide when heated at its melting point, and its solution in aqueous sodium bicarbonate decolorised permanganate almost instantaneously. The latter property is a somewhat singular one in a saturated acid, but is not infrequent in monosubstituted cyanoacetic acids; and it is for this reason that the constitution above suggested is preferred to the alternative one.

† No other method of hydrolysis tried was found so satisfactory as the above somewhat complicated one. On hydrolysis of the original additive product with sodium hydroxide, the last traces of ammonia were driven off only on prolonged boiling; in this case the product is a mixture of phenylsuccinic acid and  $\alpha$ -carboxy- $\beta$ -phenylsuccinic acid, and to obtain a homogeneous product it was found necessary to heat it to 180°, at which temperature carbon dioxide is readily lost by the carboxy-derivative (Alexander, *Annalen*, 1890, 238, 67). The calcium salts of these two acids are too soluble to be of much use in isolating the acids:



*Preparation of Phenylsuccinic acid directly from Benzaldehyde, Sodium Cyanoacetate, and Potassium Cyanide.*—Experiments showed that the conditions requisite for good yields of phenylsuccinic acid are the maintenance of a very slight alkalinity during the addition of hydrogen cyanide, low concentrations, and a small excess of potassium cyanide, and the following direct process is based on these observations.

Benzaldehyde (10.6 grams = 1 mol.) was condensed with the sodium cyanoacetate made from 10 grams of monochloroacetic acid (volume = 280 c.c.) by the addition of 3 c.c. of 20 per cent. sodium hydroxide solution. At this dilution the sodium cyanophenylacrylate remained in solution. The solution was extracted with ether to remove any unchanged benzaldehyde (0.6 gram), and then, after neutralising the alkali, 9.8 grams (1.4 mols.) of potassium cyanide dissolved in 40 c.c. of water, and 10.3 grams (1 mol.) of phenol were added. A small amount of sodium cyanophenylacrylate separated, but this redissolved after a short time. After standing for twenty-four hours, the solution was made just acid to litmus with hydrochloric acid, and the phenol extracted with ether. The solution was then made barely acid to Congo-red, and the turbidity produced removed by filtering after addition of animal charcoal and shaking. On acidifying strongly, an oil was precipitated which was hydrolysed by means of fuming hydrochloric acid to phenylsuccinic acid. A further quantity of this acid was obtained by evaporating the mother-liquor to dryness, hydrolysing with fuming hydrochloric acid, again evaporating to dryness, and extracting the residue with acetone. The total weight of phenylsuccinic acid obtained was 11.6 grams, a yield of 69 per cent. calculated on the net weight of benzaldehyde used.\*

Time has not permitted of the working out of a satisfactory process on similar lines for the more difficult operation of preparing piperonylsuccinic acid directly from piperonal.

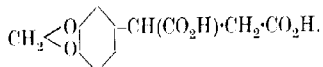
On shaking together benzaldehyde and sodium cyanoacetate with a little sodium hydroxide until the reaction as previously described took place, neutralising the alkali, and adding potassium cyanide solution containing some free hydrogen cyanide, the resulting product, under certain conditions, was a tarry oil, from which no phenylsuccinic acid could be obtained. In one experiment there was isolated from the oily reaction product, obtained by the acidifi-

\* Phenol was used in this and other experiments as a means of controlling the alkalinity of the solution; unlike more powerful acids, it has little tendency to expel hydrogen cyanide from its salts, but converts free potassium hydroxide into the slightly alkaline potassium phenoxide. It is therefore a convenient "buffer" compound for this and many other hydrogen cyanide additive processes.

cation of the foregoing mixture, a crystalline acid, forming prisms melting and decomposing at  $167^{\circ}$  (Found: C = 72.3; H = 5.5; N = 12.4; equiv. = 331.  $C_{20}H_{17}O_2N_3$  requires C = 72.2; H = 5.1; N = 12.7 per cent.; equiv. = 331). An examination of this formula leads to the opinion that the substance has been formed from the interaction of two molecules of benzaldehyde, two of cyanoacetic acid, and one of hydrogen cyanide with loss of one molecule of carbon dioxide.

The substance is readily soluble in ethyl or methyl alcohol, moderately soluble in acetone, and sparingly soluble in ether, benzene, or light petroleum. On boiling with sodium hydroxide, ammonia is quickly evolved, but the products of hydrolysis have not been closely examined.

(2) *Addition of Hydrogen Cyanide to  $\alpha$ -Cyano- $\beta$ -piperonylacrylic Acid. Preparation of Piperonylsuccinic Acid,*



The addition of hydrogen cyanide to cyanopiperonylacrylic acid takes place, as Jones showed, with one-eighth the speed of the reaction when cyanophenylacrylic acid is used at the same dilution. Further, on account of the relatively small solubility of sodium cyanopiperonylacrylate, it is better to work with dilute solutions. On the other hand, as the acid or its sodium salt is not very sensitive to small concentrations of alkali, the solution in this case may be warmed very gently to accelerate the addition. The isolation of the additive product was a simple matter, but as its hydrolysis with fuming hydrochloric acid led to carbonisation, doubtless due to the sensitive methylenedioxy-group, the alternative, slower alkaline hydrolysis, had to be used.

(a)  $\alpha$ -Cyano- $\beta$ -piperonylacrylic acid (21.7 grams), suspended in 500 c.c. of water (temperature  $40^{\circ}$ ), was dissolved by the addition, in small quantities, of a  $N$ -sodium hydroxide, avoiding much excess of alkali at any time. With this solution there was mixed a solution made by dissolving 10.5 grams (1.5 mol.) of potassium cyanide in 40 c.c. of water and adding to it 20 grams (1.1 mol.) of glacial acetic acid in 10 c.c. of water. A heavy precipitate of sodium (or potassium) cyanopiperonylacrylate was thrown down, which redissolved very slowly, its rate of solution being a rough measure of the speed of the hydrogen cyanide addition. The mixture, in a stoppered flask, was kept at about  $40^{\circ}$  for about eight days until all the precipitated salt had redissolved. The solution was made almost acid to Congo-red, and the tarry deposit separated. After adding an excess of hydrochloric acid, a turbidity was produced, which

on aspirating collected as a heavy oil. Continued aspiration caused this oil to become semi-solid, but did not bring about any further precipitation. The main portion of the additive product was obtained by evaporation on the water-bath until crystallisation began. As the product showed a marked tendency to form supersaturated solutions from which it was not easy to prepare the pure crystalline material, it was hydrolysed directly to piperonylsuccinic acid. The yield of crude product was about 75 per cent. of the theoretical.\*

(b) The additive product just described was dissolved in 20 per cent. sodium hydroxide and boiled until evolution of ammonia ceased. This proved to be a rather lengthy proceeding. The solution was then acidified and boiled for some time with animal charcoal. From this solution, after filtering hot, a mixture of piperonylsuccinic acid and its carboxy-derivative crystallised on cooling, a further portion being secured by extraction of the mother-liquor with ether. The mixture was converted into piperonylsuccinic acid by heating in an oil-bath at  $210-220^{\circ}$  until evolution of carbon dioxide ceased. The product was dissolved in sodium hydroxide solution, precipitated by means of hydrochloric acid, redissolved by boiling with water, and again heated with animal charcoal. From this hot solution, after filtration, piperonylsuccinic acid separated, on cooling, in fine needles. After several recrystallisations from hot water, it melted constantly at  $211^{\circ}$ . The yield was 80–85 per cent. of the theoretical amount (Found: C = 55.4; H = 4.1; equiv. = 118.  $C_{11}H_{10}O_6$  requires C = 55.4; H = 4.2 per cent.; equiv. = 119).

*Piperonylsuccinic acid* is readily soluble in methyl alcohol, ethyl alcohol, acetone, or acetic acid. It is soluble with difficulty in benzene, more readily soluble in hot benzene, and is almost insoluble in light petroleum. From a moderately strong solution of the sodium salt the calcium salt is precipitated on boiling after the addition of calcium chloride. The acid, when boiled with concentrated hydrochloric acid, does not exhibit the tendency to carbonise which is characteristic of the hydrogen cyanide additive product from which it is made, but with concentrated sulphuric acid it instantly darkens, showing that the methylenedioxy-group is attacked.

(3) *Attempted Addition of Hydrogen Cyanide to  $\alpha$ -Cyano- $\beta$ -styrylacrylic Acid.*—Thiele and Meisenheimer (*Annalen*, 1899, **306**, 247) obtained by the action of potassium cyanide on ethyl cinnamyl-

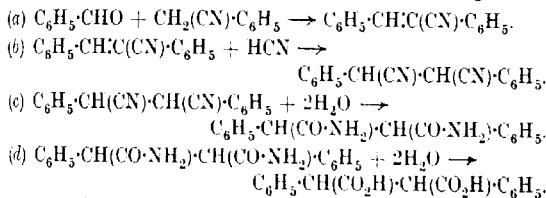
\* It has recently been found that if the ammonium salt of the unsaturated acid is used in the first instance, more concentrated solutions may be made, addition of hydrogen cyanide is accelerated, and the yield of piperonylsuccinic acid improved.

idenemalonate,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$ , a product from the hydrolysis of which they isolated only styrylsuccinic acid and that to the extent of only 13 per cent.; addition had taken place in the 1:2- and apparently not at all in the expected 1:4-positions. Hinrichsen (*Annalen*, 1904, 336, 323) endeavoured, without favourable result, to bring about the addition of hydrogen cyanide, and of other substances which enter into additive reactions with substances containing ethylenic linkings, to cyanostyrylacrylic acid, its ethyl ester, and cinnamylidenemalononitrile respectively; no details of the experiments were given, but it was stated that a variety of conditions were employed. It is thus evident that a substance containing conjugated double linkings, with one of the double linkings in the  $\alpha\beta$ -position, reacts with hydrogen cyanide, if at all, very much more slowly than does a substance with the  $\alpha\beta$ -double linking only. In view of the results of Thiele and Meisenheimer, and of the fact that the free acids are always less reactive than their esters, it is not surprising that the present authors were unsuccessful in bringing about the union of hydrogen cyanide and cyanostyrylacrylic acid.

In concluding this section, it may be mentioned that a number of experiments were made in the hope of effecting addition of the elements of hydrogen cyanide to citronellylidenecyanoacetic acid. It was clear, however, that not only does the condensation of citronellal with sodium cyanoacetate give a very mixed product and poor yields of the required unsaturated acid (compare Tiemann, *Ber.*, 1899, 32, 824), but that the conversion of the latter is attended with unusual difficulties.

*An Improved Process for Preparing s-Diphenylsuccinic Acid.*

The steps involved in the process used are the following:



No one of these is new in principle, but the processes (b), (c), and (d) have now been either simplified in technique or improved as to yield.

Step (a), the condensation of benzaldehyde with benzyl cyanide, has already been elaborated by Walther (*J. pr. Chem.*, 1896, [iii], 53, 454) to afford practically quantitative yields.

Step (b), the conversion of  $\alpha$ -phenylcinnamonitrile into *s*-diphenylsuccinonitrile, is essentially that first used by one of us (T., 1903, 83, 995), but has been modified as follows.

$\alpha$ -Phenylcinnamonitrile (20.5 grams) is dissolved in 600 c.c. of 90 per cent. ethyl alcohol by warming at 40–50°. A solution of 27.4 grams (2.5 mols.) of potassium cyanide in 80 c.c. of water is then added and the temperature of the whole maintained at 40–50°. Crystals of the sparingly soluble diphenylsuccinonitrile begin to separate slowly in the course of thirty minutes. At the end of an hour a solution of 12 grams of acetic acid in 50 c.c. of water is introduced gradually at the bottom of the solution by means of a thistle-funnel drawn out to a small aperture. The mixture is then kept at room temperature for twenty-four hours. The crystalline diphenylsuccinonitrile is separated, pressed thoroughly, and washed twice with small quantities of ether to remove any unchanged  $\alpha$ -phenylcinnamonitrile. The weight obtained is 21.3 grams (87 per cent. of the calculated). (A further small quantity can be obtained by diluting the mother-liquor, but the material thus obtained is much more impure.) The diphenylsuccinonitrile obtained in this way is pure enough for conversion into the corresponding acid. A portion, recrystallised from hot acetic acid, had a melting-point of 225° and therefore was the mixture of the stereoisomeric  $\alpha$ - and  $\beta$ -forms as noted by Chalanay and Knoevenagel (*Ber.*, 1892, 25, 1892) and by Lapworth (*loc. cit.*). Chalanay and Knoevenagel have shown that in the hydrolysis of this mixture with hydrochloric acid, only *meso*diphenylsuccinic acid is produced. Instead of using acetic acid to reduce the alkalinity of the solution, phenol dissolved in alcohol may be used equally well, but not, apparently, hydrochloric acid.

Step (c).—The hydrolysis of *s*-diphenylsuccinonitrile to *s*-diphenylsuccin diamide can be effected with excellent results as follows. [The direct conversion of the nitrile into the acid by the use of concentrated hydrochloric acid in sealed tubes at 200°, recommended by Reimer (*Ber.*, 1881, 14, 1802) and since applied by numerous workers, is not convenient for large quantities.]

*Hydrolysis of s-Diphenylsuccinonitrile to s-Diphenylsuccin diamide.*—Diphenylsuccinonitrile is dissolved in fifteen to twenty times its weight of 90 per cent. sulphuric acid by warming on the water-bath and the solution, after standing a few hours, is diluted slowly with water until no further precipitate is produced, the volume necessary being about five-fourths that of the sulphuric acid taken. The precipitate produced is of a fine, crystalline character, but if the sulphuric acid solution is poured into water or if much more water is added than seems to be necessary for complete precipitation,

a slimy precipitate separates which can be filtered only with much difficulty. The precipitated amide is collected, washed with water, and then with dilute sodium carbonate solution to remove any diphenylsuccinic acid, and finally with water. The yield is about 85 per cent. of the calculated, the remaining 15 per cent. representing presumably the amount hydrolysed to the acid.\*

Step (d).—The conversion of *s*-diphenylsuccindiamide into *s*-diphenylsuccinic acid is most readily carried out by a method which in principle was first used by Claus (*Annalen*, 1891, 266, 283), namely, by heating with 50–70 per cent. sulphuric acid; it is important that the latter concentration should not be exceeded, otherwise the acid is partly converted into diphenesuccindone (Reimer, *Ber.*, 1881, 14, 1802; Rosen, *Annalen*, 1888, 247, 152).

A clear solution is made by warming diphenylsuccindiamide on the steam-bath with fifteen to twenty times its weight of 90 per cent. sulphuric acid. (It is simple to obtain this solution directly from the nitrile; in this case diphenylsuccinonitrile is merely dissolved in fifteen to twenty times its weight of 90 per cent. sulphuric acid and kept for twelve hours.) The whole is cooled and water cautiously added until the precipitate just ceases to be redissolved on shaking even when the temperature is raised to that of the steam-bath. The whole is now heated at 120–125°. The solution, initially clear, begins to deposit diphenylsuccinic acid after a short time, and after about five hours hydrolysis is complete; but the operation should be prolonged until a test portion forms a clear solution in excess of dilute alkali, when the whole may be cooled and diluted slowly until no further precipitation takes place. The precipitate is collected, dissolved in dilute alkali, and the solution filtered and acidified. The yield of acid thus obtained is nearly quantitative.

Recrystallisation of this acid is not easy owing to its sparing solubility in most solvents, but ethyl or amyl alcohol may be used for this purpose. The crude acid may simply be boiled with acetic

\* The diphenylsuccindiamide was recrystallised several times from hot glacial acetic acid, in which it is not very freely soluble. Under the microscope it is apparently a single substance, only one of the stereoisomerides being present. It is reasonable to conclude that it is the *meso*-form which is present, since by the hydrolysis of the mixture of  $\alpha$ - and  $\beta$ -, or *r*- and *meso*-diphenylsuccinonitriles by means of hydrochloric acid only  $\beta$ - or *meso*-diphenylsuccinic acid is produced. Further, by the prolonged heating of the mixture of  $\alpha$ - and  $\beta$ -diphenylsuccinonitriles with glacial acetic acid, apparently the  $\alpha$ -form changes into the  $\beta$ -form (Found: N, 10.34. Calc., N = 10.45 per cent.).

*meso*-Diphenylsuccindiamide crystallises in microscopic, hexagonal prisms, which soften at 295° and melt at 310°. It is insoluble in benzene, light petroleum, or ether, very slightly soluble in acetone or ethyl alcohol, slightly soluble in cold acetic acid, and more so in hot acetic acid.

acid, which removes traces of coloured materials always present, and the substance is then pure enough for most purposes. A sample of the acid recrystallised from hot ethyl alcohol melted at 229°, showing that it was the *meso*-variety, and the identity of the acid was confirmed by titration.\*

*meso*-Diphenylsuccinic anhydride (Tillmanns, *Annalen*, 1890, 258, 87; Anschütz and Bendix, *ibid.*, 1890, 259, 6; Wren and Still, T., 1915, 107, 1449), heated at 150–175° with resorcinol and powdered zinc chloride, reacts to give a melt which dissolves in dilute sodium hydroxide, giving an orange-red solution with intense green fluorescence. When *m*-diethylaminophenol is used in place of resorcinol, a substance of the rhodamine type is produced, as shown when the melt is treated with alcohol, a red solution with brown fluorescence being obtained, but secondary decompositions seem to occur very readily, possibly due to the formation of diphenesuccindone derivatives.

*s*-Diphenylsuccinimide,  $\begin{matrix} \text{CHPh}\cdot\text{CO} \\ | \\ \text{CHPh}\cdot\text{CO} \end{matrix} > \text{NH}$ .—The dry ammonium salt of diphenylsuccinic acid was heated under reduced pressure, when crude diphenylsuccinimide passed over at 170–230°/13 mm. and was recrystallised several times from hot benzene. It crystallises in minute needles which soften at 194° and melt at 198° (Found: N = 5.6.  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$  requires N = 5.6 per cent.).

The substance is readily soluble in alcohol, ether, acetic acid, or acetone, sparingly soluble in cold benzene, more soluble in hot, and very slightly soluble in light petroleum.

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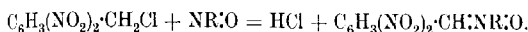
\* Other methods of conversion of the diamide into the acid were tried, such as those depending on treatment in strong sulphuric acid solution with sodium nitrite (Bouveault, *Bull. Soc. chim.*, 1892, [iv], 9, 368; Sudborough, T., 1895, 87, 601), or, better, with a stream of methyl nitrite. The results were not unpromising, but as much inconvenience arose from frothing of the solutions on dilution and as the same result was more simply achieved as above, these methods were not fully worked out.

(CV.—*N*-Oximino-ethers. Part II. *N*-Aryl Ethers of  
2 : 4- and 2 : 6-Dinitrobenzaldoximes.

By FRED BARROW, EVAN DALTON GRIFFITHS, and  
EDWARD BLOOM.

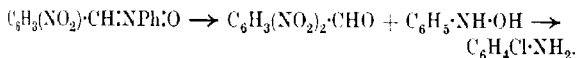
IN Part I of this investigation (Barrow and Griffiths, T., 1921, **119**, 212) it has been shown that *p*-nitrobenzyl chloride readily condenses with nitrosobenzene and its derivatives, in the presence of alcoholic potassium hydroxide, yielding *N*-aryl ethers of *p*-nitrobenzaldoxime. The investigation has been extended by the authors to other nitro-substituted benzyl haloids, and, in the present communication, the behaviour of 2 : 4- and 2 : 6-dinitrobenzyl chlorides is described.

The condensation of aromatic nitroso-compounds with 2 : 4-dinitrobenzyl chloride, under the influence of alcoholic potassium hydroxide, proceeds even more readily than is the case with *p*-nitrobenzyl chloride, yielding *N*-aryl ethers of 2 : 4-dinitrobenzaldoxime :



That these condensation products possess the constitution of *N*-oximino-ethers has been established by an examination of the behaviour of the *N*-phenyl ether, prepared from 2 : 4-dinitrobenzyl chloride and nitrosobenzene, toward hydrochloric acid.

On treatment with hydrochloric acid in acetic acid solution the *N*-phenyl ether is converted at the ordinary temperature into 2 : 4-dinitrobenzanilide, 2 : 4-dinitrobenzaldehyde, and *p*-chloroaniline. The last two compounds are produced by the normal hydrolysis of the oximino-ether to the aldehyde and  $\beta$ -phenylhydroxylamine, the latter being subsequently transformed, by the further action of the hydrochloric acid, into *p*-chloroaniline :



The simultaneous formation of 2 : 4-dinitrobenzanilide is evidently due to the oximino-ether undergoing the Beckmann transformation under the influence of the hydrochloric acid.

In the case of 2 : 6-dinitrobenzyl bromide, the condensation with nitroso-compounds is best effected by means of sodium ethoxide in anhydrous alcoholic solution. The resulting 2 : 6-dinitrobenzaldoxime-*N*-aryl ethers are unstable in the presence of aqueous alkalis and therefore cannot be obtained in a crystalline condition if the condensation is carried out by means of alcoholic potassium hydroxide in the usual manner.



## EXPERIMENTAL.

*2:4-Dinitrobenzaldoxime-N-phenyl Ether*,  $C_6H_3(NO_2)_2 \cdot CH:NPh:O$ .—Equimolecular proportions of nitrosobenzene (5.5 grams) and 2:4-dinitrobenzyl chloride (10.9 grams), prepared by Escales's method (*Ber.*, 1904, 37, 3599), were dissolved in alcohol (125 c.c.), and to the solution was added slightly more than the theoretical amount of potassium hydroxide (2.8 grams), dissolved in methyl alcohol (20 c.c.). On the addition of the alkali, the colour of the solution at once changed from green to reddish-brown, and the oximino-ether separated as a yellowish-brown powder. After remaining for one hour, this was filtered, freed from potassium chloride by washing with water, and crystallised from alcohol, the yield being 10.7 grams.

*2:4-Dinitrobenzaldoxime-N-phenyl ether* crystallises in lustrous, slender, pale yellow needles, which melt at  $149^\circ$  (Found: C = 54.43; H = 3.22; N = 14.83.  $C_{13}H_9O_5N_3$  requires C = 54.35; H = 3.14; N = 14.63 per cent.). It is very readily soluble in chloroform, moderately soluble in alcohol or benzene, and almost insoluble in ether or light petroleum.

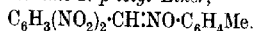
*Hydrolysis*.—Four grams of the *N*-phenyl ether, dissolved in glacial acetic acid (30 c.c.), were treated with 15 c.c. of concentrated hydrochloric acid, diluted with an equal volume of water. After remaining for one hour, the mixture was cooled in ice, the yellow solid, which separated, was removed, and the filtrate diluted with water and extracted several times with ether. On evaporation, the ethereal solution gave a red oil, which was decolorised by boiling with charcoal in alcoholic solution. It then readily crystallised, melted at  $81^\circ$ , and was identified as 2:4-dinitrobenzaldehyde. The solution, from which the 2:4-dinitrobenzaldehyde had been separated, was rendered alkaline by the addition of sodium hydroxide; the *p*-chloroaniline thus liberated was extracted with ether and its identity established by conversion into the acetyl derivative, melting at  $175^\circ$ . The yellow solid, which separated from the acetic acid solution during the hydrolysis of the *N*-phenyl ether, crystallised from alcohol in long, slender, straw-coloured needles, melting at  $193^\circ$ , and consisted of 2:4-dinitrobenzanilide (Found: C = 54.2; H = 3.23; N = 15.07.  $C_{13}H_9O_5N_3$  requires C = 54.35; H = 3.14; N = 14.63 per cent.).

For the purpose of comparison, the anilide was prepared directly from 2:4-dinitrobenzoyl chloride and a slight excess of aniline. After crystallisation from alcohol, it melted at  $193^\circ$  and was identical with that obtained above.

*Condensation of 2:4-Dinitrobenzaldehyde and  $\beta$ -Phenythydrozyl-*

*mine*.—Equimolecular proportions of the two components were heated in alcoholic solution for half an hour on the water-bath. The solid, which separated, crystallised from alcohol in slender, yellow needles melting at 150°, and was identical with the *N*-phenyl ether obtained by the condensation of 2:4-dinitrobenzyl chloride and nitrosobenzene.

2:4-Dinitrobenzaldoxime-*N*-*p*-tolyl Ether,

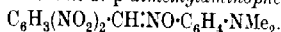


—This was prepared by the gradual addition of the theoretical amount of methyl-alcoholic potassium hydroxide (1.1 grams in 3 c.c.) to an alcoholic solution (85 c.c.) of 2:4-dinitrobenzyl chloride (4.35 grams) and *p*-nitrosotoluene (2.7 grams). Excess of potassium hydroxide must be avoided, otherwise a very impure, dark coloured product will be obtained.

The oximino-ether separated as a greenish-yellow powder, which was washed with water and crystallised from alcohol. It forms golden, silky needles melting at 167°, and is readily soluble in chloroform, less soluble in benzene or alcohol, and only very sparingly soluble in ether or light petroleum (Found C = 55.74; H = 3.51; N = 14.05.  $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}_3$  requires C = 55.81; H = 3.65; N = 13.95 per cent.).

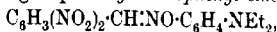
2:4-Dinitrobenzaldoxime-*N*-*o*-tolyl ether, prepared in a similar manner from *o*-nitrosotoluene, crystallises from alcohol in pale yellow leaflets melting at 225° (Found: N = 14.02.  $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}_3$  requires N = 13.95 per cent.).

2:4-Dinitrobenzaldoxime-*N*-*p*-dimethylaminophenyl Ether,



—2:4-Dinitrobenzyl chloride (10.9 grams) and *p*-nitrosodimethylaniline (7.5 grams) were dissolved in alcohol (150 c.c.) and the condensation effected in the usual manner by the addition of methyl-alcoholic potassium hydroxide (2.8 grams in 21 c.c.). The oximino-ether that separated was washed with water to remove potassium chloride, and crystallised from a mixture of equal parts of alcohol and pyridine. It forms small, dark red needles melting at 194° and is only slightly soluble in alcohol, moderately soluble in benzene, very readily soluble in pyridine or chloroform, and almost insoluble in ether or light petroleum (Found: N = 16.63.  $\text{C}_{15}\text{H}_{14}\text{O}_5\text{N}_4$  requires 16.96 per cent.). The yield amounted to 90 per cent. of the theoretical.

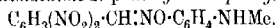
The corresponding *N*-*p*-diethylaminophenyl ether,



was prepared from *p*-nitrosodiethylaniline and purified in the same manner. It crystallises in small, very dark red leaflets, which melt at 177° with decomposition, and have about the same solubility

in the common solvents as the dimethylaminophenyl ether (Found:  $N = 15.67$ .  $C_{17}H_{18}O_5N_4$  requires  $N = 15.64$  per cent.).

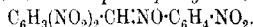
2 : 4-Dinitrobenzaloxime-N-p-methylaminophenyl Ether,



—This was obtained in almost theoretical yield by the condensation of *p*-nitrosomethylaniline and 2 : 4-dinitrobenzyl chloride. It crystallises from a mixture of equal parts of pyridine and alcohol in small, chocolate-red needles, melting at  $189^\circ$ , and is only slightly soluble in alcohol, more readily soluble in benzene, and very readily soluble in chloroform or pyridine (Found:  $N = 17.52$ .  $C_{14}H_{12}O_5N_5$  requires  $N = 17.72$  per cent.).

The corresponding N-p-ethylaminophenyl ether was prepared from *p*-nitrosoethylaniline in the same manner; it crystallises in small lustrous, dark reddish-brown leaflets melting at  $168-171^\circ$  with decomposition, and has approximately the same solubility in the common solvents as the methylaminophenyl ether (Found:  $N = 17.38$ .  $C_{15}H_{14}O_5N_4$  requires  $N = 16.96$  per cent.).

2 : 4-Dinitrobenzaloxime-N-p-nitrophenyl Ether,



—This compound was prepared in the usual manner from *p*-nitro-nitrosobenzene, the yield being 70 per cent. of the theoretical. It crystallises from alcohol in small, dark orange leaflets melting at  $155-158^\circ$  with decomposition, and is moderately soluble in alcohol or benzene, readily soluble in chloroform, and only very sparingly soluble in light petroleum or ether (Found:  $N = 17.0$ .  $C_{13}H_8O_7N_4$  requires  $N = 16.86$  per cent.).

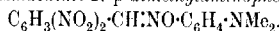
The corresponding N-m-nitrophenyl ether, prepared from *m*-nitro-nitrosobenzene, separates from a mixture of equal parts of pyridine and alcohol in slender, yellow leaflets, melting at  $225^\circ$  (Found:  $N = 16.90$ .  $C_{13}H_8O_7N_4$  requires 16.86 per cent.).

2 : 6-Dinitrobenzaloxime-N-phenyl Ether,  $C_6H_3(NO_2)_2 \cdot CH:NPbO$ .

—The 2 : 6-dinitrobenzyl bromide required for this and the following condensations was prepared by heating 2 : 6-dinitrotoluene (10 grams), bromine (10 grams), magnesium carbonate (3 grams), and a little pyridine (0.2 c.c.) for five hours in a sealed tube at  $150^\circ$  (compare Reich and Oganessian, *Bull. Soc. chim.*, 1917, [iv], **21**, 117). In several experiments in which the pyridine was omitted, the 2 : 6-dinitrotoluene was recovered unchanged. 2.7 Grams of 2 : 6-dinitrobenzyl bromide and 1 gram of nitrosobenzene, dissolved in 25 cc. of anhydrous alcohol, were treated with the theoretical amount of sodium ethoxide (0.22 gram of sodium in 6 c.c. of alcohol). On the addition of the ethoxide, the solution at once changed from green to deep red. After remaining for half an hour, the alcohol was removed at as low a temperature as possible by evaporation

under diminished pressure, and the residue extracted with hot benzene. The oximino-ether, obtained by removing the benzene under diminished pressure, was purified by crystallisation from alcohol. It separates as a pale yellow powder melting at  $138^{\circ}$ , and is moderately soluble in alcohol or benzene, very readily soluble in chloroform or pyridine, and only very sparingly soluble in ether and light petroleum (Found:  $N = 14.42$ .  $C_{13}H_9O_5N_3$  requires  $N = 14.63$  per cent.).

2:6-Dinitrobenzaloxime-N-p-dimethylaminophenyl Ether,



This was prepared from *p*-nitrosodimethylaniline and 2:6-dinitrobenzyl bromide in a similar manner to that described above. It crystallises from alcohol in short, deep red prisms, which melt at  $161^{\circ}$ , with decomposition (Found:  $N = 17.15$ .  $C_{15}H_{11}O_5N_4$  requires  $N = 16.96$  per cent.).

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## LXVI.—The Formation of Derivatives of Tetrahydronaphthalene from $\gamma$ -Phenyl Fatty Acids. Part II.\*

By ARNOLD STEVENSON and JOCELYN FIELD THORPE.

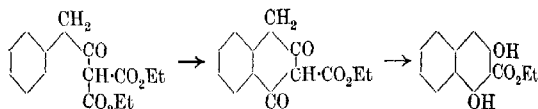
In Part I of this series, it was shown that the formation of the second (hydrogenated) ring in a derivative of tetra-hydronaphthalene, as distinct from the production of the naphthalene nucleus itself, seemed to depend on the presence of substituting groups on the carbon atoms of the side chain and it was shown, in particular, that the attachment of groups to the  $\beta$ -carbon atom (in respect of the benzene ring) produced a profound effect on ring closure.

Experiments have now been continued, because it is intended in this series thoroughly to investigate the effect of substitution at different positions on the side chain in order if possible, by comparing the conditions of ring closure with those of the fully saturated carbon ring systems, now being investigated in these laboratories, to draw some conclusion as to the stereochemical configuration of the benzene nucleus.

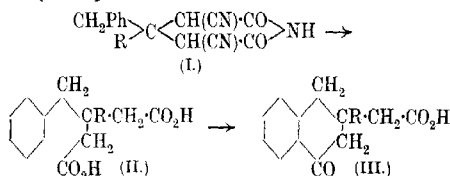
A number of examples are known of the formation of tetra-hydronaphthalene derivatives from compounds having a benzene nucleus to which is attached a side chain of four carbon atoms. A compound of this type may be the derivative of an acid, as, for instance,  $\gamma$ -phenylbutyryl chloride, which reacts with aluminium

\* Part I appeared T., 1921 119, 87.

chloride (Kipping and Hill, T., 1889, **75**, 144) to form 1-ketotetrahydronaphthalene, or ethyl phenylacetylmalonate, which when treated with sulphuric acid (Metzner, *Annalen*, 1897, **298**, 374) passes through a tetrahydronaphthalene derivative into ethyl 1:3-dihydroxynaphthalene-2-carboxylate:

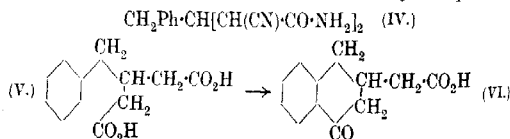


There appear, however, to be only two cases recorded in which an actual acid, as distinct from its derivative, undergoes a change of this type, the closing of the ring being effected through the elimination of a molecule of water formed from the hydroxyl group of the acid and one hydrogen atom of the benzene nucleus in the ortho-position. Kon and Stevenson (T., 1921, **119**, 87) found that the imides derived by Guareschi's method from ethyl and methyl benzyl ketones on hydrolysis gave tetrahydronaphthalene derivatives, which were no doubt formed in accordance with scheme (a), although it was not found possible to isolate the intermediate dibasic acids (II), this being probably due to the fact that a hydrolysing agent (sulphuric acid) sufficiently strong to cause the fission of the imide ring is powerful enough to eliminate water and form the tetrahydronaphthalene derivative.

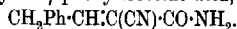


Scheme (a).

This fission of the imide ring could be avoided by using Day and Thorpe's method (T., 1920, **117**, 1465) for the production of  $\beta$ -substituted glutaric acids, so that by condensing phenylacetaldehyde with cyanoacetamide it should be possible to form the diamide of  $\alpha\alpha'$ -dieryano- $\beta$ -benzylglutaric acid (IV), which on hydrolysis should give  $\beta$ -benzylglutaric acid (V). From this the tetrahydronaphthalene



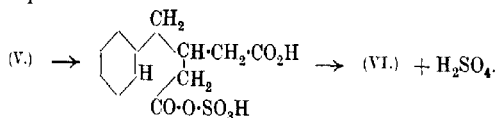
derivative (VI) should be obtained by the elimination of a molecule of water. Unfortunately, Day and Thorpe found that while their method gave excellent results with aliphatic compounds, aromatic aldehydes on condensation with cyanoacetamide formed unsaturated compounds, a conclusion borne out by the preliminary experiments on phenylacetaldehyde already described (Kon and Stevenson, *loc. cit.*), in which only traces of the diamide (IV) were obtained. It has, however, now been found that under proper conditions the yield of diamide in the condensation product can be increased to 10 per cent. of the theoretical, the major part consisting of the amide of  $\alpha$ -cyano- $\gamma$ -phenylcrotonic acid,



Phenylacetaldehyde would thus appear in its behaviour towards cyanoacetamide to be intermediate between the aliphatic and the aromatic aldehydes.

It was found that the diamide (IV) on hydrolysis with hydrochloric or moderately dilute sulphuric acid gave  $\beta$ -benzylglutaric acid (V) (Vorländer and Strunck, *Annalen*, 1906, **345**, 239), and that this on treatment with concentrated sulphuric acid at room temperature passed almost quantitatively into the tetrahydronaphthalene derivative (VI), the constitution of which was proved by the formation of a semicarbazone and by the production of phthalic acid on oxidation with potassium permanganate. This reaction therefore furnishes an example of the direct formation of a tetrahydronaphthalene derivative from a  $\gamma$ -phenylbutyric acid through the elimination of a molecule of water.

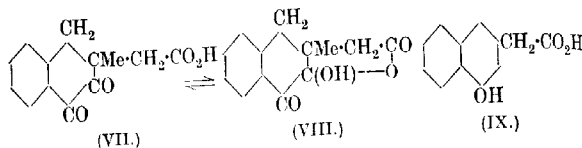
When heated at  $180^\circ$ , the open chain acid (V) remains unchanged and if treated with a dehydrating agent such as acetyl chloride (Vorländer and Strunck, *loc. cit.*) loses water to form the anhydride. It is therefore remarkable that sulphuric acid should eliminate water in a different way and close the tetrahydronaphthalene ring. This action must be due to the formation in the first place of a sulphuric acid ester, which then loses sulphuric acid to form the ring complex :



This explanation of the reaction will have to be taken into account when the general survey of the field is made at the end of this series.

Although the acid (VI) closely resembles in its general properties the homologue containing a methyl group (III), there is a marked

difference between them in their behaviour on regulated oxidation with potassium permanganate. The latter readily passes (Kon, Stevenson, and Thorpe, this vol., p. 652) into a stable compound which exists in the two tautomeric forms (VII) and (VIII):



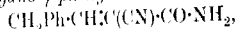
The presence of a methyl group attached to a quaternary carbon atom no doubt prevents the elimination of hydrogen and the consequent production of a naphthalene derivative and so allows the formation of the oxidation product (VII and VIII). The acid (VI) on similar treatment yielded no homologous compound, but formed a tar characteristic of those obtained from naphthalene, whilst an attempt to regulate the oxidation so as to obtain the substituted naphthol (IX) merely gave a mixture of tar and parent acid.

## EXPERIMENTAL.

### *Condensation of Phenylacetaldehyde with Cyanoacetamide.*

Phenylacetaldehyde readily polymerises on keeping and this leads to unsatisfactory yields on condensation with cyanoacetamide. The polymerisation can, however, be prevented by at once adding to freshly prepared aldehyde about twice its weight of absolute alcohol. To 23 grams of phenylacetaldehyde in 50 c.c. of alcohol another 200 c.c. of alcohol were added and then a solution of 80 grams of cyanoacetamide in 400 c.c. of water, a few drops of piperidine being also added to act as a condensing agent. The mixture was well shaken in a wide-mouthed stoppered bottle for about half an hour, when a precipitate had formed. After keeping for twelve hours, it was filtered off and extracted with hot alcohol. 4.5 Grams of the insoluble diamide of  $\alpha\alpha'$ -dicyano- $\beta$ -benzylglutaric acid were obtained and this was found to decompose and melt at 249°.\*

The amide of  $\alpha$ -cyano- $\gamma$ -phenylcrotonic acid,



is deposited in clusters of needles as the filtrate cools, the yield being about 23 grams. After rubbing with ethyl acetate and twice crystallising from alcohol, the amide softened at 202° and melted

In the preliminary experiments (*loc. cit.*) the melting point was given as 245°.

at 207° (Found : C = 70.55; H = 5.51; N = 15.16.  $C_{11}H_{10}ON_2$  requires C = 70.93; H = 5.43; N = 15.05 per cent.).

*β-Benzylglutaric Acid (V).*

Twenty c.c. of concentrated hydrochloric acid were added to 6 grams of the diamide of  $\alpha\alpha'$ -dicyano- $\beta$ -benzylglutaric acid, and the mixture diluted with 10 c.c. of water and heated under reflux for two to three hours. When cold, it was extracted with ether, the ethereal extract yielding 3 grams of the crude acid. Crystallised from benzene, it separated in stout prisms which melted at 99–101° (Found : C = 64.79; H = 6.41. Calc., C = 64.84; H = 6.35 per cent.). In order to ascertain if hydrolysis with moderately dilute sulphuric acid (45 per cent. by volume) would close the tetrahydronaphthalene ring, 5 grams of diamide were heated under reflux with 100 c.c. of acid till evolution of gas ceased. After dilution, it was extracted with ether, and from the ethereal extract there were obtained 2 grams of product rather dark in colour. After twice crystallising from benzene and light petroleum, it melted sharply at 101° and proved to be  $\beta$ -benzylglutaric acid [Found : C = 64.61; H = 6.51 per cent. Titration with  $N/10$ -sodium hydroxide. Found : 14.1 c.c. Calc. (dibasic), 13.9 c.c.].

*ac-1-Ketotetrahydronaphthalene-3-acetic Acid (VI).*

Three grams of  $\beta$ -benzylglutaric acid were dissolved at room temperature in 15 c.c. of concentrated sulphuric acid. After keeping over-night, the solution was poured on to ice and extracted with ether, the ethereal extract yielding 2.4 grams of crude condensation product. This was purified by converting it into its semicarbazone, regenerating by warming with 25 per cent. sulphuric acid, and extracting with ether. Crystallised from benzene, it formed prisms which sintered at 109° and melted at 110–111° [Found : C = 70.91; H = 5.83.  $C_{12}H_{12}O_3$  requires C = 70.55; H = 5.93 per cent. Titration with  $N/20$ -sodium hydroxide. Found : 13.95 c.c. Calc. (monobasic), 14.30 c.c.]. The acid can also be prepared by heating the parent acid under reflux with sulphuric acid (60 per cent. by volume), but this method gives a less pure product. The silver, cupric, lead, ferric, and aluminium salts are readily formed in the cold from the ammonium salt, whilst the calcium salt is obtained as a gelatinous precipitate on boiling the neutral sodium salt for some time with calcium chloride solution.

The *semicarbazone* was readily prepared by mixing an alcoholic solution of the acid with semicarbazide acetate solution. It is very sparingly soluble in alcohol, separating as a crystalline powder



## 1722 FORMATION OF DERIVATIVES OF TETRAHYDRONAPHTHALENE.

melting at  $238^{\circ}$  (Found:  $N = 16.22$ .  $C_{13}H_{15}O_3N_3$  requires  $N = 16.09$  per cent.).

The oxidation to phthalic acid was carried out by dissolving 3 grams of the acid in sodium hydroxide solution, heating on the steam-bath, and adding a warm saturated solution of potassium permanganate until the colour persisted. After destroying the excess of permanganate with sulphurous acid, the solution was filtered, and the filtrate acidified and extracted with ether, the ethereal extract yielding crude phthalic acid. Crystallised from water and rubbed with ether and then with alcohol, it melted and decomposed at  $203^{\circ}$  and on heating with resorcinol gave fluorescein [Titration with  $N/20$ -sodium hydroxide. Found: 17.3 c.c. Calc. (dibasic), 17.2 c.c.].

For the regulated oxidation the method employed for the preparation of the tautomeric substance (VII and VIII) was followed. Three grams of the acid were dissolved in sodium hydroxide solution, and a 1 per cent. solution of potassium permanganate added until the colour persisted, the operation being carried out at a temperature of about  $10^{\circ}$ . The excess of permanganate was destroyed with sulphurous acid and the solution filtered, acidified, concentrated by evaporation, and extracted with ether, the ethereal extract yielding a brown, tarry substance which could not be crystallised. In order to ascertain if the naphthalene derivative (IX) could be obtained, 1 gram of the acid was dissolved in sodium hydroxide solution, and potassium permanganate added sufficient for the oxidation of two hydrogen atoms. Treated as above, a tar was obtained from which, on addition of lead nitrate, the lead salt of an acid was obtained. On regeneration and crystallisation, this acid proved to be identical with the parent acid.

We are indebted to the Chemical Society for a grant which has partly paid for the materials used in the investigation, and to Messrs. W. J. Bush & Co., Ltd., for supplying us with freshly prepared phenylacetaldehyde.

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CCVII.—*Researches on Residual Affinity and Co-ordination. Part IX. Cobaltammine Salts of the Nitro-Dyes.*

By GILBERT T. MORGAN and HERBERT JOSEPH SEYMOUR KING.

It has been shown that the mordant dyes of the quinoneoxime and alizarin series contain chelate groups which can enter into the co-ordination sphere of cobaltamines, displacing completely the ammonia (Morgan and Main Smith, T., 1921, 119, 708; this vol., p. 165). This investigation is being extended to mordant dyes of the azo-series, and the results so far obtained show that these colouring matters also owe their capacity for forming metallic lakes to the presence in their molecules of at least one chelate group, which is identified by its power of saturating completely the chemical affinity of trivalent cobalt so that a stable complex containing this metallic atom is produced with three chelate groups taking the place of the six ammonias in hexamminocobaltic salts. This property is in all probability a distinctive feature of organic mordant dyes, but in order to establish the generalisation it becomes necessary to ascertain whether substantive dyes behave similarly or differently towards cobaltamines.

The object of the present investigation was to determine whether the substantive nitro-dyes furnish chelate groups when combined with the cobaltamines, and for this purpose four typical nitro-dyes were examined: picric acid, dipicrylamine (aurantia or imperial yellow), 2:4-dinitro- $\alpha$ -naphthol (naphthol yellow N), and 2:4-dinitro- $\alpha$ -naphthol-7-sulphonic acid (naphthol yellow S).

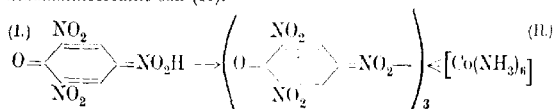
The salts of these colouring matters containing chloropentammino-, quopentammino-, and hexammino-cobaltic radicles were prepared and found to be sparingly soluble compounds quite stable at the ordinary temperature. On heating at 95° under reduced pressure, these salts evolved a certain amount of ammonia, but only in one instance did the loss amount to two-fifths of the total quantity present in the compound. In other cases this loss was considerably less.

The behaviour on heating of the cobaltammine salts of the substantive nitro-dyes stands in marked contrast to the behaviour of the cobaltammine salts of nitroso- $\beta$ -naphthol. The latter series lose their ammonia completely even at 50° and become transformed into cobaltic 1-nitroso- $\beta$ -naphthoxide (cobaltic 1:2-naphthaquinone-1-oximate), a stable insoluble lake in which the metallic atom remains solely combined with three chelate groups of the mordant quinoneoxime dye.

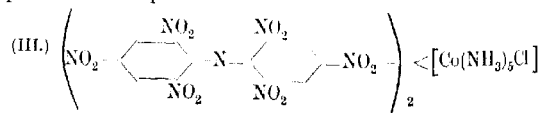
<i>Mordant Dyes.</i>	Percentage NH <sub>3</sub> before heating.	Percentage NH <sub>3</sub> after heating.	Percentage lost.
<i>Cobaltamines.</i>			
Hexamminocobaltic 1 : 2-naphthaquinone-1-oximate .....	14.56	0	100
Chloropentamminocobaltic 1 : 2-naphthaquinone-1-oximate .....	Unstable at room temperature		99
(T., 1921, <i>loc. cit.</i> ).			
<i>Substantive Nitro-dyes.</i>			
Chloropentamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide .....	11.78	11.41	3.14
Chloropentamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide-7-sulphonate ..	16.26	16.00	1.60
Hexamminocobaltic dipicrylamine ..	6.73	6.53	2.97
Hexamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide .....	11.04	10.76	2.54
Hexamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide-7-sulphonate .....	15.09	13.83	8.35
Aquopentamminocobaltic picrate .....	9.95	6.12	38.49
Aquopentamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide .....	9.54	9.46	0.84
Aquopentamminocobaltic dipicrylamine	6.31	5.66	10.30

The foregoing table indicates that the cobaltamine salts of the nitro-dyes are comparatively stable even on heating. In no case has ammonia been displaced either partly or completely by the nitro-groups.

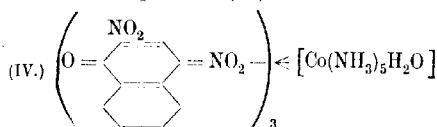
The experimental results described below show that, unlike the mordant dyes of the quinoneoxime, alizarin, and hydroxyazo-series the substantive nitro-dyes do not furnish chelate groups each capable of reacting as two associating units in the co-ordination sphere of a cobaltic atom. This behaviour of the nitro-dyes may be assigned to a lack of residual affinity in the nitro-groups as regards cobalt or it may be taken as corroborative evidence of the para-quinonoid configuration of the nitro-dyes, the following formulae showing the relationship between picric acid (I) and its hexamminocobaltic salt (II).



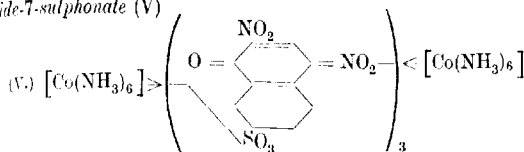
The quinone hypothesis would also account for the complete absence of co-ordination between cobalt and nitro-groups in chloropentamminocobaltic dipicrylamine (III), since the co-ordination complex and the nearest nitro-groups are now in meta-positions with respect to each other.



Similar considerations applied to the naphthol yellows would lead to the following formulations (IV and V) for *aquopentamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide* (IV)



and for the more complex *hexamminocobaltic 2 : 4-dinitro- $\alpha$ -naphthoxide-7-sulphonate* (V)



Pieric acid, dipicrylamine, and 2 : 4-dinitro- $\alpha$ -naphthol have given a complete series of purpureo-, roseo-, and luteo-salts containing respectively the complete co-ordination complexes  $[\text{CoCl} \cdot 5\text{NH}_3]$ ,  $[\text{Co}5\text{NH}_3 \cdot \text{H}_2\text{O}]$ , and  $[\text{Co}6\text{NH}_3]$ .

The purpureo- and luteo-salts of 2 : 4-dinitro- $\alpha$ -naphthol-7-sulphonic acid were also prepared, but the roseo-salt was obtained only in association with silver chloride as formed by double decomposition between roseo-cobaltic chloride and the silver salt of the nitro-sulphonic acid. But in no case was any experimental evidence forthcoming that the associating units of the three foregoing complexes had been displaced by substituent groups derived from the nitro-colouring matters.

#### EXPERIMENTAL.

The cobaltammines described below, which were prepared from the purified nitro-dyes and from cobaltammine salts of ascertained composition, were precipitated at room temperature and kept in the cold mother-liquor until collected, when they were washed repeatedly with dilute ammonia and finally with water. These products were then dried in a vacuum desiccator containing soda-lime and ammonium carbonate, and finally kept for three hours under reduced pressure over concentrated sulphuric acid.

##### I. Cobaltammines of Pieric Acid.

The cobaltammine pierates were crystalline compounds, sparingly soluble in cold water to yellow solutions; on warming, the dissolved salt underwent partial hydrolysis.

1. *Chloropentamminocobaltic pierate* separated in reddish-brown

needles (4 grams) on adding 2.74 grams of chloropentamminocobaltic chloride in 650 c.c. of water to 5 grams of picric acid in 500 c.c. of water containing 22 c.c. of *N*-sodium hydroxide (Found: Co = 9.56;  $\text{NH}_3$  = 13.29; N = 23.87; Cl = 5.45.  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \{ \text{C}_6\text{H}_2(\text{NO}_2)_3\text{O} \}_2$  requires Co = 9.28;  $\text{NH}_3$  = 13.40; N = 24.24; Cl = 5.58 per cent.). The formation of this compound is referred to by Jörgensen (*J. pr. Chem.*, 1878, **18**, 232) and by Ephraim (*Ber.*, 1921, **54**, [B], 402), but no analyses have hitherto been recorded.

2. *Aquopentamminocobaltic picrate* was precipitated in masses of small, yellow needles (4.1 grams) on adding slowly 1.6 grams of aquopentamminocobaltic chloride in 25 c.c. of water to 12 grams (9 mols.) of picric acid dissolved in 52.5 c.c. of *N*-sodium hydroxide and 700 c.c. of water (Found: Co = 7.30;  $\text{NH}_3$  = 9.95; N = 22.73;  $\text{H}_2\text{O}$  = 2.11.  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \{ \text{C}_6\text{H}_2(\text{NO}_2)_3\text{O} \}_3$  requires Co = 6.97;  $\text{NH}_3$  = 10.06; N = 23.17;  $\text{H}_2\text{O}$  = 2.13 per cent.).

3. *Hexamminocobaltic picrate* (formula II) was obtained in a state of purity only by employing an excess (6 mols.) of picric acid; 5 grams of this reagent were dissolved in 21.9 c.c. of *N*-sodium hydroxide in 500 c.c. of water and treated slowly with 1.27 grams of hexamminocobaltic nitrate in 75 c.c. of water, when clusters of sulphur-yellow needles were forthwith precipitated (2.5 grams) (Found: Co = 6.95;  $\text{NH}_3$  = 12.24; N = 24.60.  $[\text{Co}(\text{NH}_3)_6] \{ \text{C}_6\text{H}_2(\text{NO}_2)_3\text{O} \}_3$  requires Co = 6.98;  $\text{NH}_3$  = 12.09; N = 24.86 per cent.). This salt has been referred to recently by Ephraim, but only a partial analysis is given (*Ber.*, 1922, **55**, [B], 1615).

## II. Cobaltamines of Dipicrylamine.

The cobaltamine salts of dipicrylamine were obtained as red, non-crystallisable solids rather more soluble in cold water than the cobaltamine salts of the other nitro-dyes.

1. *Chloropentamminocobaltic Dipicrylamine* (Formula III).—Three grams of dipicrylamine converted into ammonium salt and dissolved in 900 c.c. of water were treated with 0.86 gram of chloropentamminocobaltic chloride in 230 c.c. of water, when a granular, crimson precipitate was deposited (Found: Co = 5.60;  $\text{NH}_3$  = 7.79; N = 25.06; Cl = 3.04.  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \{ \text{C}_{12}\text{H}_9\text{O}_{12}\text{N}_7 \}_2$  requires Co = 5.59;  $\text{NH}_3$  = 8.07; N = 25.21; Cl = 3.36 per cent.).

2. *Aquopentamminocobaltic Dipicrylamine*.—Aquopentamminocobaltic chloride (0.37 gram) in 20 c.c. of water was added slowly to 2.9 grams (4.5 mols.) of dipicrylamine dissolved in 6.6 c.c. of *N*-sodium hydroxide and 700 c.c. of water; the product (1 gram) was a bright red powder somewhat soluble in

water (Found : Co = 4.22;  $\text{NH}_3$  = 6.31; N = 24.86;  $\text{H}_2\text{O}$  = 2.75.  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \{ \text{C}_{12}\text{H}_4\text{O}_{12}\text{N}_7 \}_3 \cdot 3\text{H}_2\text{O}$  requires Co = 3.95;  $\text{NH}_3$  = 5.70; N = 24.37;  $\text{H}_2\text{O}$  = 2.41 per cent.).

3. *Hexamminocobaltic Dipicrylamine*, a scarlet compound of lighter shade than the two preceding salts, was obtained by adding 1.05 grams of hexamminocobaltic nitrate to 8 grams (6 mols.) of dipicrylamine in 18.2 c.c. of *N*-sodium hydroxide and 400 c.c. of water (Found : Co = 4.27;  $\text{NH}_3$  = 6.73; N = 24.64;  $\text{H}_2\text{O}$  = 2.90.  $[\text{Co}(\text{NH}_3)_6] \{ \text{C}_{12}\text{H}_4\text{O}_{12}\text{N}_7 \}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  requires Co = 3.88;  $\text{NH}_3$  = 6.72; N = 24.88;  $\text{H}_2\text{O}$  = 2.96 per cent.).

### III. Cobaltamines of 2 : 4-Dinitro-*x*-naphthol.

The three following compounds are identical in colour, being orange when wet and brick red on drying; they are obtained as pasty, non-crystalline precipitates very sparingly soluble in cold water to yellow solutions. When dried at the ordinary temperature, they are found on analysis to be hydrated, but although the amount of water is variable, the ratio of cobalt to ammonia is consistent with the absence of co-ordination between cobalt and the nitro-groups.

1. *Chloropentamminocobaltic 2 : 4-Dinitro-*x*-naphthoxide*.—Chloropentamminocobaltic chloride (1.61 grams) in 550 c.c. of water was added to 3 grams of 2 : 4-dinitro-*x*-naphthol dissolved in 12.8 c.c. of *N*-sodium hydroxide and 1 litre of water, when 2.2 grams of the product were precipitated (Found : Co = 8.61;  $\text{NH}_3$  = 11.84; N = 18.11; Cl = 4.61;  $\text{H}_2\text{O}$  = 8.50.  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \{ \text{C}_{10}\text{H}_5\text{O}_5\text{N}_2 \}_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  requires Co = 8.32;  $\text{NH}_3$  = 12.01; N = 17.79; Cl = 5.00;  $\text{H}_2\text{O}$  = 8.90 per cent.).

2. *Aquopentamminocobaltic 2 : 4-Dinitro-*x*-naphthoxide* (Formula IV).—Two grams of 2 : 4-dinitro-*x*-naphthol dissolved in 8.5 c.c. of *N*-sodium hydroxide and 700 c.c. of water were treated with 0.765 gram of aquopentamminocobaltic chloride in 20 c.c. of water (Found : Co = 6.86;  $\text{NH}_3$  = 9.54; N = 16.94;  $\text{H}_2\text{O}$  = 5.10.  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \{ \text{C}_{10}\text{H}_5\text{O}_5\text{N}_2 \}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Co = 6.64;  $\text{NH}_3$  = 9.59; N = 17.34;  $\text{H}_2\text{O}$  = 5.07 per cent.).

3. *Hexamminocobaltic 2 : 4-Dinitro-*x*-naphthoxide*.—Three grams of 2 : 4-dinitro-*x*-naphthol, dissolved in 12.8 c.c. of *N*-sodium hydroxide and one litre of water, were treated with 1.48 grams of hexamminocobaltic nitrate in 150 c.c. of water, when the product was easily filtered, although if excess of the sodium salt was employed filtration and washing became impossible even with the aid of a centrifuge (Found : Co = 6.80;  $\text{NH}_3$  = 11.04; N = 18.58;  $\text{H}_2\text{O}$  = 3.43.  $[\text{Co}(\text{NH}_3)_6] \{ \text{C}_{10}\text{H}_5\text{O}_5\text{N}_2 \}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Co = 6.61;  $\text{NH}_3$  = 11.46; N = 18.85;  $\text{H}_2\text{O}$  = 3.53 per cent.).

IV. Cobaltamines of 2:4-Dinitro- $\alpha$ -naphthol-7-sulphonic Acid.

It was not found possible to prepare monocobaltamine salts of naphthol yellow S even when using a large excess of its sodium salt. This behaviour is in agreement with the observation of Knecht and Hibbert (*Ber.*, 1904, **37**, 3475) that a monopotassium salt is not obtainable. The following dicobaltamine salts are orange, crystalline, hydrated compounds, sparingly soluble in water to yellow solutions.

1. *Chloropentaminocobaltic 2:4-Dinitro- $\alpha$ -naphthoxide-7-sulphonate*.—Four grams of 2:4-dinitro- $\alpha$ -naphthol-7-sulphonic acid in 250 c.c. of water were converted into the ammonium salt and treated with 2.72 grams of chloropentaminocobaltic chloride in 600 c.c. of water, when the product separated in small, orange needles (Found: Co = 11.50;  $\text{NH}_3$  = 16.26; N = 18.85; Cl = 6.34; S = 6.25;  $\text{H}_2\text{O}$  = 4.84.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2 \cdot \text{C}_{10}\text{H}_4\text{O}_8\text{N}_2\text{S} \cdot 2.3\text{H}_2\text{O}$  requires Co = 11.37;  $\text{NH}_3$  = 16.42; N = 18.90; Cl = 6.84; S = 6.18;  $\text{H}_2\text{O}$  = 5.21 per cent.).

2. *Hexaminocobaltic 2:4-Dinitro- $\alpha$ -naphthoxide-7-sulphonate* (Formula V).—Six grams of 2:4-dinitro- $\alpha$ -naphthol-7-sulphonic acid, converted into the ammonium salt in 350 c.c. of water, were treated with 1.89 grams of hexaminocobaltic nitrate, when a bright yellow, crystalline precipitate was deposited, which owing to difficulties of filtration was separated and washed in a centrifuge. The product consisted of irregular plates (2.4 grams) (Found: Co = 8.68;  $\text{NH}_3$  = 15.09; N = 18.13; S = 6.79;  $\text{H}_2\text{O}$  = 7.64.  $[\text{Co}(\text{NH}_3)_6]_2 \cdot \text{C}_{10}\text{H}_4\text{O}_8\text{N}_2\text{S} \cdot 3.6\text{H}_2\text{O}$  requires Co = 8.63;  $\text{NH}_3$  = 14.95; N = 18.45; S = 7.04;  $\text{H}_2\text{O}$  = 7.91 per cent.).

Ammonia was estimated in the cobaltamine salts of the two  $\alpha$ -naphthol derivatives by distillation with aqueous sodium hydroxide, but this procedure failed in the case of the compounds derived from picric acid and dipicrylamine, as in each case the acidic radicle was decomposed and contributed a further quantity of ammonia, which was slowly evolved, so that a definite end-point could not be obtained. From the dipicrylamine compounds the ammonia evolved was more than would correspond with the nitrogen of the imino-group, and evidently as in the case of picric acid ammonia arose from a reduction of nitro-groups. The dipicrylamine derivatives were first decomposed with concentrated sulphuric acid and after diluting and filtering from dipicrylamine the ammonia in the filtrate was estimated in the ordinary way. In the cobaltamine picrates the ammonia was estimated by distilling with calcium carbonate instead of with sodium hydroxide.

The water in the hydrated compounds was not removed com-

pletely under reduced pressure over phosphoric oxide, but both water of crystallisation and co-ordinated water of the aquopent-ammino-salts were determined by heating at  $95^{\circ}$  to constant weight in a vacuum, ammonia being estimated before and after this treatment. Since these cobaltamine salts of the nitro-dyes deflagrate or explode on heating alone, cobalt was estimated by gently warming with sulphuric acid in a silica crucible. The residue contained carbon except in the case of the picrates. After strong ignition, the residual cobalt oxide was heated gently with moderately concentrated sulphuric acid, and the metal finally weighed as sulphate.

Chlorine in the complex chlorides was estimated as silver chloride produced by digesting the organic salt with fuming nitric acid and silver nitrate.

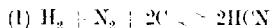
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[Received, July 14th, 1922.]

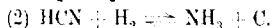
## CCVIII.—*The Explosion of Acetylene and Nitrogen.* *Part II.*

By WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO.

IN a previous paper (T., 1921, **119**, 1903), a study was made of the fixation of nitrogen which occurs when this gas is exploded with acetylene. During this process, the nitrogen is fixed almost entirely in the form of hydrocyanic acid, the explosion yielding only small amounts of ammonia. The more important reactions in the synthesis of ammonia and hydrocyanic acid were shown to be



and



The values of  $K_1$  in the equation  $K_1 = [\text{HCN}]^2/[\text{H}_2][\text{N}_2]$  were found to vary from 0.0124 with 4.13 per cent. of nitrogen to 0.0069 with 20.33 per cent. of nitrogen. On the other hand, an empirical relationship,  $[\text{HCN}]/[\text{H}_2][\text{N}_2]^{0.37} = K_1^{1/2}$ , held fairly accurately over the range of concentrations investigated, but no explanation could be given of the physical basis of the equation. Further analysis showed that another equation could be derived from this which was equally applicable. It is possible to replace the concentration of hydrogen by a factor proportional to the area of the carbon surface, for in the experiments previously reported, the atomic concentrations of the carbon and hydrogen in the explosion vessel

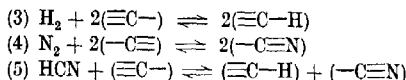


were identical. Thus  $[\text{HCN}]/[\text{C}][\text{N}_2]^{0.37} = K_1^{\text{II}}$ . Further experimental work was, however, necessary before a decision could be made as to the relative merits of these two alternatives.

In the study of the reactions occurring in gaseous explosions, the rate of cooling of the gaseous products is a factor of considerable importance and it was desirable to ascertain if  $K_1^{\text{I}}$  or  $K_1^{\text{II}}$  held for different rates of cooling of the gaseous products. The evidence already obtained on this point was fairly definite, for in the previous experiments the temperature of explosion and the rate of cooling were progressively altered by the addition of increasing amounts of nitrogen to the explosive mixture, without producing any variations in the value of these constants. Since, however, it was possible that this concordance was accidental, further alterations in the conditions of firing were made by the addition of hydrogen and helium to the mixtures of acetylene and nitrogen. A material increase in the rate of cooling is brought about by the substitution of either of these gases for nitrogen. The thermal conductivities of hydrogen and helium at  $0^\circ$  are 0.0003386 and 0.0003270 respectively, values which are very similar and about six times as large as that of nitrogen (0.000057). Although the effect of these two gases on the rates of cooling will be almost identical, their effect on the temperatures of explosion will be very different. On account of the low specific heat of helium, the temperatures of explosion will be higher in the presence of this gas than when equal amounts of either nitrogen or hydrogen are present.

The substitution of helium for a portion of the nitrogen was found to be without effect on  $K_1^{\text{I}}$ , although this constant was lowered about 10 per cent. by the addition of 10 per cent. of hydrogen (Table II). If, however, the hydrogen concentration in this equation be replaced by a quantity proportional to the amount of carbon present, as in  $K_1^{\text{II}} = [\text{HCN}]/[\text{C}][\text{N}_2]^{0.37}$ , where  $[\text{C}]$  represents the atomic concentration per litre of carbon in the bomb, then it is found that  $K_1^{\text{II}} = 0.079$  for all of the experiments within experimental error. This agreement suggests that the quantities of hydrocyanic acid produced in these explosions are practically independent of the partial pressures of the hydrogen, being a function only of the carbon surface and the nitrogen concentration. This case is analogous to those observed by Langmuir (*Trans. Faraday Soc.*, 1922, **17**, 621) in the reactions between hydrogen and oxygen, and carbon monoxide and oxygen on a platinum surface. It was observed that when either of the two reactants was present in excess the velocity of the reaction was independent of the partial pressure of this reactant and proportional solely to the partial pressure of the other reactant.

The more important reactions, occurring on the carbon surface, may be written



The reaction between carbon and hydrogen (3) is more energetic than that between carbon and nitrogen (4). At  $800^\circ$ , the adsorption of hydrogen by carbon is considerable, whereas nitrogen is not appreciably absorbed at this temperature.\* At high temperatures ( $1800$ — $1900^\circ$ , the temperature of chilling of the hydrocyanic acid reactions), the equilibrium density of hydrogen atoms in the interface will be established with great rapidity, and it seems probable that at high partial pressures the hydrogen atoms will occupy the majority of the *free* spaces on the carbon surface, and that the density of packing will change only slightly with variations in the partial pressure of the gas. If the formation of hydrocyanic acid occurs between the nitrogen and hydrogen atoms on the surface (5) or on collision between nitrogen molecules and the adsorbed hydrogen atoms, then it would be expected that the rate of formation of hydrocyanic acid would be practically independent of the partial pressure of the hydrogen, a conclusion which is in agreement with the experimental results.

In order to test these ideas still further, the ratio of carbon to hydrogen in the gas mixture was increased by the addition of cyanogen to the acetylene. Owing, however, to the incomplete decomposition of the cyanogen which was present in the cooler regions of the bomb and the production of hydrocyanic acid secondarily by the action of hydrogen on cyanogen, it was impossible to draw any conclusions from these results.

An unexpectedly low result was obtained for the percentage of ammonia produced during the explosion of mixtures containing helium. In the experiments with an excess of hydrogen the average value for  $[\text{NH}_3]/[\text{H}_2][\text{HCN}] = K_2$  was  $0.51$ , and the mean for comparable experiments obtained previously (*loc. cit.*) was  $0.42$ . In the helium series, the constant was  $0.31$ , the mean of three experiments (see last column, Table II). It is difficult to ascribe this result to differences between the rates of cooling, or between the temperatures of explosion of the mixtures in the various series. Previous work had shown that the alteration in these conditions brought about by dilution of the acetylene with nitrogen is without appreciable effect on the value of  $K_2$ .

In view of the work of (Sir) J. J. Thomson, it is possible that

\* Unpublished experiments by Mr. E. A. Blench.

helium acts as a negative catalyst. Positively charged molecules of hydrogen with the noble gases are known to exist under the conditions prevailing in a positive-ray tube. The formation of such a compound between a positively charged hydrogen atom and a helium atom would explain the negative catalysis. If the hydrogen atoms which are active in the production of ammonia are positively charged, then the reduction in concentration of these atoms, occurring on collision with helium atoms, would lower the rate of production of ammonia from hydrocyanic acid or from hydrogen and nitrogen. Experimental work is in progress to test these ideas.

#### EXPERIMENTAL.

In all, three series of experiments were carried out. Mixtures containing (1) acetylene, nitrogen, and helium, (2) acetylene, nitrogen, and hydrogen, and (3) acetylene and cyanogen were exploded in a spherical vessel at a pressure of approximately three atmospheres. The force of explosion, on account of the dilution with inert gases, was not sufficiently great to cause leaks at the main joint of the bomb, a difficulty which was experienced in some of the earlier experiments. No essential modifications have been made in the apparatus (Fig. 2, *loc. cit.*) or in the experimental procedure, except that it has been found possible to dispense with the bubblers *C*.

(a) *Materials*.—The supply of helium was kindly presented by Dr. Travers from a quantity obtained from Prof. Moore, of the Bureau of Mines. This gas was purified by passing over heated copper oxide and through coconut charcoal cooled in liquid air. The densities of the gas used in four experiments were 4.008, 3.998, 3.982, and 4.002, respectively. The hydrogen was obtained from zinc and sulphuric acid and was purified over charcoal, surrounded by liquid air. Considerable loss occurred in this process, until the carbon was saturated with hydrogen. Cyanogen, obtained by the action of heat on dry mercuric cyanide (Dixon, T., 1886, 49, 384), was purified by passing over cotton wool moistened with silver nitrate and dried over phosphoric oxide. The sources of the nitrogen and acetylene have already been given in a previous paper.

(b) *Analysis*.—When helium was present in the final gaseous mixture, slight alterations were necessary in some of the analytical methods. In the determination of hydrogen by the copper oxide method, owing to the ready diffusion of helium through the quartz tube, it was necessary to replace this material by hard glass. The analysis of the residue of nitrogen and helium also presented some

difficulty. These gases were sparked with excess of oxygen in order to remove the nitrogen, but the results came out too low. On this account it was decided to calculate the percentage of these gases in the final mixture from the initial composition. For this purpose the density of the helium was carefully determined beforehand and accurately known volumes of helium and nitrogen were measured into the bomb.

The cyanogen in the gases was analysed by passing a known volume of the gas through a solution of sodium hydroxide and titrating the solution with silver nitrate by Denigès's method. The analyses by this method were in good agreement with the quantities of cyanogen measured into the bomb. As the gases from the explosion of mixtures of cyanogen and acetylene contained unchanged cyanogen, it was important to devise methods of analysing mixtures containing ammonia, hydrocyanic acid, and cyanogen. The following method of procedure was adopted. The gases were passed through dilute sulphuric acid ( $N/10$ ) and sodium hydroxide solutions in a series of bubblers, the cyanogen being converted into a mixture of cyanide and cyanate in the alkaline solution. The cyanogen and hydrocyanic acid dissolved in the dilute sulphuric acid were distilled off into a solution of sodium hydroxide and the ammonia in the acid solution was analysed. It has been shown previously that hydrocyanic acid is not appreciably hydrolysed by this treatment. Experiments with cyanogen showed that less than 2 per cent. of this gas was converted into ammonia during the distillation with sulphuric acid. The alkaline solution was titrated for cyanide by Denigès's method. The cyanate in this solution was determined after the removal of the hydrocyanic acid by distillation with excess of dilute sulphuric acid. The residue was treated with more sulphuric acid (Wallis, *Annalen*, 1906, **345**, 357), the cyanate converted into an ammonium salt, and the ammonia analysed by the ordinary methods. 30.61 C.c. of cyanogen gave 28.69 c.c. of ammonia and 28.08 c.c. of hydrocyanic acid. Part of this discrepancy (6 per cent.) was caused by polymerisation of the cyanogen in the presence of mercury in the gas burette. On account of this discrepancy the analysis of the cyanogen in the *final* gases in Table I cannot be relied on to within 6 per cent. or about 0.02 per cent. of the total volume of gases present. The agreement between the two values for the nitrogen percentage shows that but little error can have occurred in the analysis of the initial gas mixture. As it was decided not to continue these experiments with cyanogen, the cause of the loss of 6 per cent. in the above analysis was not further investigated.

*Results.*

Table I contains the experimental data, the volume of gases, and the analyses of the initial and final gases. The volume of the gases given in this table is that measured after the explosion, this being the more accurate value, since the gaseous products are more "perfect" than the gases before the explosion. On account of the uncertainty in the values for the compressibility of acetylene, the pressures of the gases measured before the explosion were made use of only as a rough check on the accuracy of mixing of the gases.

Two series of values are given for the percentage of nitrogen; the first is obtained by gas analysis and the second is calculated from the percentage of nitrogen originally present in the bomb; the nitrogen converted into ammonia and hydrocyanic acid is deducted. The former nitrogen percentage is usually somewhat higher (column 16), but the latter (column 17) is the more accurate and is used in the calculations.

The acetylene in the final gases varies between 1 and 4 per cent., and owes its origin very largely to the amount of the explosive mixture which escapes decomposition in the neighbourhood of the walls of the bomb. This conclusion is supported by the results of the explosions of cyanogen and acetylene. In these experiments, 2 to 4 per cent. of the cyanogen and the same percentage of the original acetylene escaped decomposition. The high percentages of the hydrocyanic acid and ammonia in this series are possibly due to direct combination between undecomposed cyanogen and hydrogen.

*Comparison of Results.*

The effects of the addition of helium and hydrogen to the gaseous mixture of acetylene and nitrogen are summarised in Table II. Here the concentrations of the carbon, hydrogen, and nitrogen are given in gram-mols. per litre. The values from four series are included in this table, (1) the experiments V, VIII, VI, IV, and IX of the preceding paper on the explosion of mixtures of acetylene and nitrogen, (2) the helium series, (3) the hydrogen series, and (4) the cyanogen series.

(a) *The Hydrocyanic Acid Equilibrium.*—The effect of the replacement of hydrogen by carbon in the relation  $[\text{HCN}]/[\text{H}_2][\text{N}_2]^{0.37} = K_1^1$  is shown in columns 5 and 6. The modified expression gives values for  $K_1^{11}$  for the first three series which agree within experimental error, the mean values being for (1) 0.0803, (2) 0.0790, and for (3) 0.0775. The addition of 10 per cent. of hydrogen or helium is almost without effect on the latter constant.

No. of expt.	Initial gases (at atm. press.) Per cent.	Final gases. Per cent.			
		$C_2H_2$	$H_2$	$(CN)_2$	$H_2$ obs. $H_2$ calc. $N_2$ obs. $N_2$ calc.
Helium series	1	12.370	8.44	—	78.14 78.35 7.52 7.55
	2	12.370	8.44	—	79.02 79.03 7.97 7.86
	3	12.303	8.83	—	78.19 77.91 7.38 7.65
	4	12.297	8.83	—	81.55 81.85 6.15 5.76
Hydrogen series	1	12.943	9.04	—	86.84 87.00 8.11 7.86
	2	13.698	8.81	—	86.92 87.23 8.04 7.86
	3	13.100	81.77	—	88.42 88.63 7.07 6.46
	4	13.486	80.88	—	83.67 83.92 10.52 10.12
Cyanogen series	1	11.680	90.11	—	0.446 83.88 83.97 7.89 7.60
	2	13.416	90.19	—	0.232 84.56 84.61 8.19 7.86

\* Acid accidentally mixed with alkali.

TABLE II.

No. of expt.	Concentration in mols./litre.	$[HCN]^*$		$[H_2][N_2]^{0.5}$		$[NH_3]$	
		$[HCN]$	$[N_2]$	$[HCN]$	$[N_2]$	$[H_2]$	$[HCN]$
Series I	VIII	0.244	0.0116	0.0806	0.0803	0.41	—
	VI	0.259	0.0122	0.0796	0.0784	0.39	—
	IV	0.240	0.0151	0.0821	0.0820	0.44	0.42
	IX	0.231	0.0157	0.0814	0.0812	0.44	—
Helium series	1	0.217	0.0100	0.0814	0.0813	0.25	—
	2	0.220	0.0109	0.0778	0.0777	0.32	0.31
	3	0.224	0.0110	0.0814	0.0812	0.37	—
	4	0.225	0.0079	0.0760	0.0759	0.37	—
Hydrogen series	1	0.225	0.0114	0.0700	0.0784	0.46	—
	2	0.242	0.0116	0.0694	0.0767	0.54	0.51
	3	0.230	0.0098	0.0700	0.0790	0.50	—
	4	0.231	0.0153	0.0694	0.0759	0.55	—
Cyanogen series	1	0.245	0.0099	—	0.1027	0.51	—
	2	0.284	0.0186	—	0.0859	0.71	—

\* The concentrations are expressed in gram-mols. per litre. This was not done for the values of  $K_1$  given in the previous paper.

(b) *The Ammonia Equilibrium.*—The mean values for  $[\text{NH}_3]/[\text{H}_2][\text{HCN}] = K_2$  differ markedly for the different series, being 0.42 for series 1, 0.31 for series 2, and 0.51 for series 3. The addition of helium decreases and the addition of hydrogen increases the value of  $K_2$ . The results of the cyanogen are of doubtful value.

*Summary.*

Mixtures of acetylene and nitrogen with hydrogen and helium, and of acetylene with cyanogen have been exploded and the products analysed. The yield of hydrocyanic acid is given by the relation  $[\text{HCN}] = K_1^{11}[\text{C}][\text{N}_2]^{0.37}$ . The constant  $K_1^{11} = 0.079$  is found to hold for the experiments previously reported and for the mixtures containing hydrogen and helium. The concentrations of ammonia, produced during the explosion, are given approximately by the equation  $[\text{NH}_3] = K_2[\text{HCN}][\text{H}_2]$ .  $K_2$  is decreased by the addition of helium and increased by the addition of hydrogen to the gaseous mixture. Helium thus acts as a negative catalyst. The mixtures of cyanogen and acetylene gave larger amounts of ammonia and hydrocyanic acid than those normally obtained; this was accompanied by the presence of unchanged cyanogen in the gases after the explosion.

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# CCIX.—*The Adsorption of Uranium-X and its Isotope, Thorium, by Basic Ferric Acetate.*

By ANDREW CHARLES BROWN.

THE study of the adsorption of radioactive substances is a valuable aid to the investigation of the phenomenon of adsorption on a solid surface at a solid-liquid interface. By it one is enabled to examine adsorption at that most interesting stage where the first layer of atoms or molecules is being laid down.

The use of dyes in very dilute solution, using colorimetric methods of observation, has met with fair success, but by the use of radioactive substances it is possible to work with greater accuracy at much smaller concentrations.

Freundlich's empirical formula for adsorption is

$$x/m := ac^{1/n},$$

where  $x$  is the amount adsorbed,  $m$  the amount of adsorbing substance,  $c$  is the end concentration in the solution,  $a$  is an arbitrary

constant the value of which depends on the nature of the substances in question and the units used;  $1/n$ , according to Freundlich, is always less than 1, generally between 0.1 and 0.5, but it should have a constant value for a given substance, using the same adsorbent and solvent. The graph  $\log. x/m$  (ordinates),  $\log. c$  (abscissæ) would then be a straight line, and, provided the same scale is chosen for ordinates and abscissæ, the gradient would equal  $1/n$ .

An examination of published results, however, throws doubt on the constancy of the value of  $1/n$ .

Biltz (*Ber.*, 1904, **37**, 3138) and, more recently, Boswell and Dickson (*J. Amer. Chem. Soc.*, 1918, **40**, 1793) investigated the adsorption of arsenious acid by ferric hydroxide. The latter, in their summary, state: "The logarithmic curves plotted from our measurements, although approximating to straight lines, yet show unmistakably a concavity to the  $x$ -axis thus indicating a deviation of the adsorption phenomenon from the adsorption equation." That is, over the relatively small range of concentration examined by them, they observed the value of  $1/n$  to increase with decreasing concentration, its average value being about  $1/5$ .

Experimenting on the adsorption of dyes in very dilute solution by cotton fibres, Georgievics observed that  $C_{\text{fibre}}/C_{\text{solution}}$  is a constant (Zsigmondy, "Chemistry of Colloids," 1917, p. 205), that is, the value of  $1/n$  is 1.

Ritzel (*Z. physikal. Chem.*, 1909, **67**, 724) investigated the adsorption of uranium-X by charcoal, and found the value of the exponent  $1/n$  to be 1. He also observed that the addition of a trace of thorium prevents the adsorption of uranium-X. Now if it is accepted that uranium-X and its isotope, thorium, are not separable by an adsorption process, the value of  $1/n$  must decrease with increasing concentration of the element "atomic number 90," because if it remained equal to 1, increasing concentration would not alter the ratio of the amount of element adsorbed to that in solution.

By employing the isotopy of uranium-X and thorium, a method suggests itself for testing the adsorption formula over a very large range of concentration, and with the view of observing the alteration in value of  $1/n$ , the following series of experiments were carried out:

1. Investigation of the adsorption of uranium-X from a solution containing no thorium.
2. Investigation of the adsorption of uranium-X from solutions containing known small concentrations of thorium.

Uranium acetate was used as the source of uranium-X, and basic ferric acetate as adsorbent.



## EXPERIMENTAL.

After many preliminary experiments, it was found best to use basic ferric acetate as adsorbent.

A few drops of a ferric sulphate solution were added to a boiling solution of uranium acetate, the acidity of which had been previously adjusted, and boiled under reflux for thirty minutes. On boiling for a longer period, no alteration in the amount adsorbed was observed.

It was noticed that if the iron solution was added in the cold, less uranium-X was adsorbed. This was probably due to the colloidal particles in the latter case being larger.

The advantages of this procedure were that the conditions were quite standard and, moreover, after filtration, the solution was practically unchanged.

*Preparation of Iron Sulphate Solution.*—12.5 Grams of anhydrous ferric sulphate were dissolved in 250 c.c. of water with the addition of a little sulphuric acid to prevent hydrolysis. One c.c. of this solution was taken as unity in the determination of *m*.

*Preparation of Uranium Acetate Solution.*—Twenty-eight grams of uranium acetate,  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ , were dissolved in 600 c.c. of water and 35 c.c. of dilute sulphuric acid (10 grams per 100 c.c.), 17.5 c.c. of sodium acetate solution (30 grams per 100 c.c.) were then added, and the solution was boiled under reflux for thirty minutes. The flocculent matter which appeared was filtered off, and the volume made up to 700 c.c.

*Estimation of Total  $\beta$ -Activity.*—Twenty c.c. of this solution were diluted with 50 c.c. of water, and 5 drops of a thorium nitrate solution (1 c.c. = 0.08 gram of thorium) added. After mixing, 0.5 gram of ammonium benzoate was added, and the solution boiled under reflux for five minutes. The precipitate of thorium benzoate was immediately filtered off by suction on a double layer of ash-free filter-paper, about  $1\frac{1}{4}$  inches in diameter, supported on a porcelain plate. This was the method adopted for all subsequent filtrations.

This treatment removed about 98 per cent. of the uranium-X. A further treatment with 5 drops of thorium solution removed the remainder.

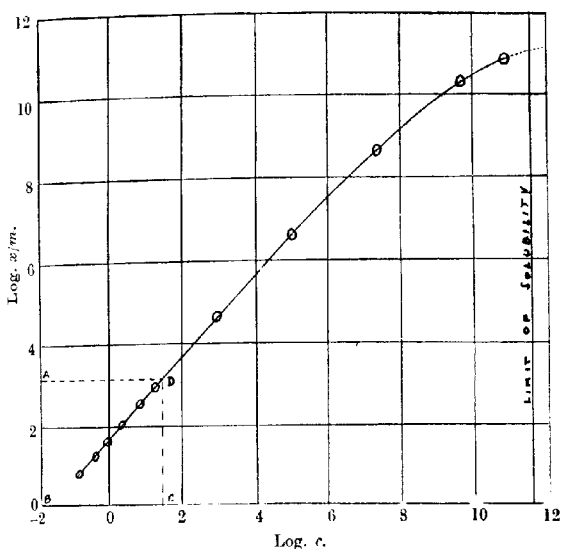
The  $\beta$ -activities of these precipitates and also of the flocculent matter were observed, corrections were made for decay between the times of precipitation and observation, and the readings standardised by comparison with a standard of uranium oxide.

$\beta$ -Activity of flocculent matter		= 67.48 div. per min.
" first ppt.	= 10.80	
" second ppt.	= 0.22	
" 700 c.c. of solution	= $11.02 \times 35 = 385.70$	
		<hr/> Total 453.18

This is the  $\beta$ -activity due to uranium-X when present in equilibrium quantity.

*Removal of Thorium if present.*—The clear solution (680 c.c.) was raised to boiling under reflux, and 1 c.c. of the iron solution was added. After boiling for thirty minutes, the solution was filtered hot. Scarcely any iron was precipitated owing to its slight solubility. A further 1 c.c. of iron solution was now added to the boiling solution, which was again boiled for thirty minutes and filtered, and a precipitate was now obtained. The treatment

FIG. 1.



with iron was repeated sixteen times. This removes any thorium which might be present together with all the uranium-X. The solution was made up to the original volume (680 c.c.) and left for several weeks to generate uranium-X.

#### *Series I. Thorium Absent.*

Five hundred and sixty c.c. of this solution were brought to boiling under reflux, 5 drops of the iron solution were added, the solution was boiled for thirty minutes, and the precipitate of basic ferric acetate filtered off. This treatment with 5 drops of iron solution was repeated six times.

The  $\beta$ -activities of these precipitates were observed. The total  $\beta$ -activity due to uranium-X was obtained by calculation from the decay curve and checked by a determination on a fresh quantity of the original solution.

The equilibrium activity after each precipitation was obtained by difference, the amount of uranium-X regenerated between experiments being taken into account; this correction was most important towards the end of the series.

The amount of adsorbent was determined with  $N/200$ -titanous chloride.

The results are given in Table I, and the graph  $\log. x/m$ ,  $\log. c$  in Fig. 1 (*ABCD*):  $m$  = amount of adsorbent (1 c.c. of iron solution = 1),  $x$  =  $\beta$ -activity of adsorbent in div. per min.,  $c_1$  = equilibrium  $\beta$ -activity in solution (500 c.c.), and  $c$  = equilibrium  $\beta$ -activity per 100 c.c. The total  $\beta$ -activity of 500 c.c. of solution at the start was 289.87 div. per min.

TABLE I.  
Series I. Thorium Absent.

Expt. No.	$m$ .	$x$ .	$c_1$ .	$c$ .	$\log. x/m$ .	$\log. c$ .
1	0.246	180.16	109.8	19.60	2.865	1.292
2	0.255	71.84	38.02	6.79	2.450	0.832
3	0.231	25.81	12.43	2.22	2.048	0.346
4	0.222	8.20	4.45	0.794	1.568	1.900
5	0.164	2.85	1.92	0.343	1.240	1.535
6	0.192	1.36	0.89	0.143	0.850	1.155
7	0.681 15 drops	1.10	—	—	0.207	—

The results obtained were fully confirmed by repetition.

*Series II. Thorium Added.*

The solution which had been used for Series I was, after keeping for some weeks, used for this series also.

The amount of uranium-X corresponding with 1 div. per min. of  $\beta$ -activity was calculated and found to be  $0.407 \times 10^{12}$  gram. One c.c. of thorium nitrate solution was found to contain 0.07575 gram of thorium. The same number of atoms of uranium-X would weigh 0.07513 gram and would give a  $\beta$ -activity of  $1.846 \times 10^{11}$  div. per min.

By successive dilution, solutions of thorium were prepared of concentrations comparable with that of the uranium-X solution. The procedure was to add the desired amount of thorium (contained in 1 c.c. of water) to 50 c.c. of the uranium-X solution of known strength and to heat the mixture to the boiling point. Ten drops of an iron solution of one-fifth the original strength were

then added, and after boiling for thirty minutes, the precipitate was filtered off and the  $\beta$ -activity and the iron determined.

The first addition of thorium was equivalent to 0.2 c.c. of the original thorium nitrate solution, which corresponds with the number of atoms of uranium-X giving a  $\beta$ -activity represented by  $3.69 \times 10^{10}$  div. per min. Fifty c.c. of the uranium-X solution had a  $\beta$ -activity represented by 24.78 div. per min., so that the concentration of the element "atomic number 90" was raised by the factor  $1.49 \times 10^9$ .

The results are recorded in Table II and depicted in the graph  $\log. x/m$ ,  $\log. c$  shown in Fig. 1. (The part of the latter enclosed by the rectangle *ABCD* is the graph for Series I.)

In Table II,  $T$  = c.c. of the original thorium nitrate solution added,  $x_1$  =  $\beta$ -activity of the adsorbent in div. per min.,  $x$  =  $\beta$ -activity of the element "atomic number 90" on the adsorbent in div. per min.,  $m$  = amount of the adsorbent (1 c.c. of the original iron solution = 1),  $c_1$  =  $\beta$ -activity, in div. per min., in the filtrate (50 c.c.), in equilibrium, and  $c$  =  $\beta$ -activity, in div. per min., of the element "atomic number 90" per 100 c.c. of filtrate in equilibrium.

The solubility limit was exceeded when  $T = 2$ , and a precipitate appeared on boiling. The activity of this precipitate was observed and the solubility limit shown in Fig. 1 obtained by calculation. It corresponded with 0.17 per cent. of thorium.

TABLE II.

## Series II. Thorium Added.

Expt. No.	$T$	$x_1$	$x \times 1.49^{-1}$	$m$	$c_1$	$c \times 1.49^{-1}$	$\log. x/m$	$\log. c$
1	—	21.50	$21.50 \times 1.49^{-1}$	0.062	3.28	6.56	1.49 <sup>-1</sup>	2.5195
2	0.2	2.27	$2.27 \times 10^8$	0.042	22.51	$45.02 \times 10^8$	10.906	10.827
3	0.02	8.88	$8.88 \times 10^8$	0.059	15.90	$31.80 \times 10^8$	10.352	9.676
4	0.0;2	17.10	$17.10 \times 10^8$	0.055	7.68	$15.36 \times 10^8$	8.666	7.360
5	0.0;2	22.03	$22.03 \times 10^8$	0.076	2.75	$5.50 \times 10^8$	6.636	4.914
6	0.0;2	21.70	$21.70 \times 10^8$	0.080	3.08	$6.16 \times 10^8$	4.696	2.963

The results were confirmed by repetition.

TABLE III.

	Series I.						Series II.				
$\log. x/m$	1	2	3	4	5	6	7	8	9	10	11
$1/n$ .....	0.97	0.97	0.96	0.96	0.97	0.97	0.92	0.87	0.77	0.65	0.44
← Limit of analysis by chemical means.											

*Results and Discussion.*

For the adsorption of uranium-X in absence of thorium, the exponent  $1/n$  was found to be 1 (Fig. 1). With the addition of

its isotope, this value was at first not affected, then, with increasing concentration, the value of  $1/n$  decreased (Fig. 1), the assumption being made that the thorium is divided between adsorbent and solution in the same ratio as the uranium-X. The values of  $1/n$  for the respective logarithms of the concentration on the adsorbent ( $x/m$ ) are shown in Table III.

At the limit of chemical means of investigation, indicated roughly by the arrow in Table III, the value of  $1/n$  is already well below 1. This explains why the addition of thorium prevents the adsorption of a detectable amount of uranium-X.

This seems to indicate that at first the potential capacity of the adsorbing surface does not alter, but, with increasing surface concentration, after a certain point it becomes weaker and weaker. Thus, for very small surface concentrations, the value of the exponent will be independent of the nature of the adsorbent, solvent, or adsorbed substance, and will be equal to 1, but with increasing surface concentration the value of the exponent will fall, and the greater the surface concentration the smaller will be the value of  $1/n$ , other factors being constant. The inability to measure the surface of the adsorbent used prevents any conclusions being drawn as to the thickness of the surface layer, but the general inferences are in agreement with Langmuir's theoretical deductions on the adsorption of gases at a surface (*J. Amer. Chem. Soc.*, 1918, 40, 1361).

The adsorption curve (Fig. 1) appears to meet the solubility limit quite uniformly, but the small activities obtaining at this point prevent this point from being established beyond doubt by this method.

Since the value of the exponent continually decreases once it has become less than 1, Freundlich's adsorption law is strictly true only when  $1/n = 1$ . When  $1/n$  is less than 1, the law is an approximation holding only over relatively small ranges of concentration. This explains the slight deviations observed by Boswell and Dickson and others, and shown by the concavity of their graphs to the  $x$ -axis.

The slow rate of change of value of  $1/n$  with increasing concentration accounts for the constant, fractional values sometimes obtained in the investigation of adsorption phenomena.

#### Summary.

1. The adsorption of uranium-X by basic ferric acetate is proportional to the concentration, and thus the exponent  $1/n = 1$ .
2. By "artificially" increasing the concentration of uranium-X by the addition of its isotope, thorium, the value of  $1/n$  is at first unchanged, but with increasing concentration its value decreases.

3. The fall in the value of the exponent with increasing concentration is in general agreement with Langmuir's theoretical deductions on the adsorption of gases at solid surfaces.

4. The decreasing value of the exponent offers an explanation of the deviations observed by Boswell and Dickson.

5. Freundlich's adsorption law is strictly true only when the exponent equals 1. For values less than 1, the law is only approximate, and the comparative constancy of the exponent observed by other investigators can be explained by the relatively small ranges of concentration over which their observations were made.

It is intended to carry out similar experiments with surfaces of known area, and more fully to investigate the part of the curve at the solubility limit.

It is a pleasure to acknowledge my indebtedness to Dr. J. A. Cranston for his instruction and advice on radioactive measurements.

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### CCX.—*The Isolation of Muscarine, the Potent Principle of Amanita muscaria.*

By HAROLD KING.

THE problem of muscarine, initiated more than half a century ago by Schmiedeberg and Koppe ("Das Muscarin," Leipzig, 1869), is one of great chemical and pharmacological interest. These workers isolated from an extract of the Fly Agaric (*Amanita muscaria*), using potassium mercuric iodide as a precipitant, a deliquescent, syrupy base with very powerful physiological properties, arresting the frog's heart in diastole in very small amounts and having an action antagonised by atropine. In 1875 Harnack (*Arch. Exp. Path. Pharm.*, 4, 168), working in the same laboratory, obtained, by fractionation of the bases as chlorides and as aurichlorides, choline aurichloride as the main and less soluble constituent, and from the mother-liquors muscarine aurichloride. On analysis of the latter, he obtained figures for carbon, hydrogen, gold, and chlorine in good agreement with  $C_5H_{14}O_2NAuCl_4$ , a substance with one oxygen atom more than choline aurichloride. To this substance Harnack and Schmiedeberg (*ibid.*, 1876, 6, 101) assigned the constitution of a hydrated aldehyde, corresponding to choline,  $(CH_3)_3NCl \cdot CH_2 \cdot CH(OH)_2$ . This was apparently substantiated by the observation that choline, when treated with pure nitric acid,

gave a "synthetic muscarine," which in its physiological properties and in the analytical values for the carbon, hydrogen, and gold of its gold salt and the platinum of its platinum salt appeared to agree with those found (in the case of the gold salt) and calculated (in the case of the platinum salt) for muscarine from *A. muscaria*. The evidence furnished by the action of nitric acid on choline was corroborated by Nothnagel (*Ber.*, 1893, **26**, 801), who described a "synthetic muscarine," and in addition the nitrous ester of choline,  $(\text{CH}_3)_3\text{NCl}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{NO}$ , as produced by this reaction.

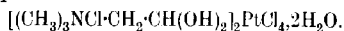
On the pharmacological side, however, Böhm (*Arch. Exp. Path. Pharm.*, 1885, **19**, 60) had already shown that the "synthetic muscarine" of Schmiedeberg and Harnack was, in reality, far weaker than natural muscarine, and, in addition, had a curare type of action on the atropinised frog, not shown by natural muscarine. This observation was completely confirmed by Hans Meyer (*Ber.*, 1893, **26**, 801), who used Nothnagel's preparations.

In 1914, Ewins (*Biochem. J.*, **8**, 209) showed clearly that the "synthetic muscarine" (pseudomuscarine) of Schmiedeberg and Harnack and of Nothnagel was identical with choline nitrous ester, the physiological action of this ester being shown by Dale to exhibit all those properties attributed to "synthetic muscarine." Choline nitrous ester and "synthetic muscarine" are, in fact, one and the same substance.

Another complication had meanwhile arisen in the synthesis by Berlinerblau (*Ber.*, 1884, **17**, 1141) and by E. Fischer (*ibid.*, 1893, **26**, 470), by different methods, of betaine aldehyde,  $(\text{CH}_3)_3\text{NCl}\cdot\text{CH}_2\cdot\text{CHO}$ . As might be expected on chemical grounds, it had one molecule of water less than the hydrated form of the aldehyde,  $(\text{CH}_3)_3\text{NCl}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})_2$ , ascribed to muscarine by Schmiedeberg and Harnack. According to Hans Meyer, the physiological action of betaine aldehyde (anhydromuscarine) was quite different from those of the natural and "synthetic muscarine," even 10 mg. failing to arrest the frog's heart.

Only two workers, Harnack and Nothnagel, claim to have isolated natural muscarine from *A. muscaria* in an analytically pure state, other workers either failing to find it (Küng, *Z. physiol. Chem.*, 1914, **91**, 241; Zellner, *Monatsh.*, 1904, **25**, 537; 1905, **26**, 727) or being mainly concerned with its pharmacology (Harmsen, *Arch. Exp. Path. Pharm.*, 1903, **50**, 361; Honda, *ibid.*, 1911, **65**, 454). Harnack prepared relatively large quantities of the gold salt, but failed to detect any difference in appearance between the choline and muscarine aurichlorides; in fact, he states that the gold salts of both muscarine and choline crystallise in short or long, prismatic, needle-shaped crystals. Nothnagel (*Diss.*, Marburg, 1893), from

350 grams of the complex mercuric iodides of the bases of *A. muscaria*, avoiding the gold salts owing to the similarity of their appearance, obtained, by prolonged fractionation of the platinum salts, 0.5 gram of muscarine platinichloride, crystallising in minute octahedra, identical in appearance with "synthetic muscarine" platinichloride (now known to be choline nitrous ester). On drying at 100°, the platinum salt showed no loss. Nevertheless, Nothnagel, having determined the platinum content by an indirect method of analysis, ascribed to the platinum salt the constitution



This is identical with the formula given by Schmiedeberg and Harnack to the platinum salt of "synthetic muscarine," and based by them on the platinum content and on a loss corresponding with 2H<sub>2</sub>O at 130—145°. Nothnagel then prepared the gold salt from the platinum salt and found that it crystallised in small leaflets.

It will be seen that the combined labours of chemists and pharmacologists had rendered untenable the *constitution* assigned by Schmiedeberg and Harnack either to natural muscarine or "synthetic muscarine." On the other hand, Nothnagel's analyses of natural muscarine might be interpreted as supporting Harnack's formula, C<sub>5</sub>H<sub>14</sub>O<sub>2</sub>NCl. Attempts have been made by Schmidt and Bode (*Annalen*, 1892, **267**, 268), Nothnagel (*loc. cit.*), and Ewins (*Biochem. J.*, 1914, **8**, 366) to synthesise muscarine by the preparation of quaternary bases of this formula, or substances of a different formula but related to cholina. The attempts, whilst producing substances of great pharmacological interest, have failed to produce a quaternary base having a muscarine action, but devoid of the nicotine-curare type of action, which is not present in natural muscarine (Dale, *J. Pharm. Expt. Ther.*, 1914, **6**, 147).

To the present author, it appeared that the only hope of further progress lay in another attempt to prepare natural muscarine, avoiding, if possible, Schmiedeberg and Koppe's precipitant, potassium mercuric iodide. This is not a really efficient precipitant, as many as three or four precipitations being necessary on the same liquor, with intermediate removal of dissolved mercuric and iodide ions. The decomposition of the precipitate, moreover, is a tedious and complicated process. In addition, rigorous physiological control at each step was a *sine quâ non*, in order to avoid loss of active material, either by decomposition or mechanically, as the amount of muscarine in *A. muscaria* was believed to be very small.

The method employed is given in its essential details in the experimental portion, the main lines being indicated here. The isolation of muscarine depends on its solubility in absolute alcohol, and on its immunity from precipitation by basic lead acetate or



colloidal iron. It was only partly precipitated with choline by aqueous mercuric chloride in neutral solution. A much larger proportion was precipitated by alcoholic mercuric chloride, and a further quantity by repeating the process after intermediate removal of some inhibitory substances. Finally, the residual muscarine was completely precipitated by phosphotungstic acid. Muscarine can also be precipitated completely by saturating with mercuric chloride in alcoholic solution, in the absence of inhibitory substances.

The distribution of active material is shown by the following table:

Aqueous HgCl <sub>2</sub> ppt. 14%	First alcoholic HgCl <sub>2</sub> ppt. 34%	Second alcoholic HgCl <sub>2</sub> ppt. 15%	Phosphotungstic acid ppt. 17%	Total recovered. 80%
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The combined precipitated bases thus obtained consist chiefly of choline and muscarine in a ratio of the order of 20 : 1, accompanied by one or more substances, of which one, at least, is laevorotatory. The major portion of the choline was separated by fractionation as the *d*-hydrogen tartrate from 95 per cent. alcohol by Honda's method, which is difficult but efficient. Fractionation was then continued by means of the aurichlorides, choline aurichloride being again the less soluble. From the mother-liquors muscarine aurichloride was finally isolated in large, delicate leaflets, totally distinct from choline aurichloride, and from Harnack's description of muscarine aurichloride, but not inconsistent with Nothnagel's description. On analysis, it was found to contain 38 per cent. of gold, whereas Harnack and Nothnagel found 43.0 and 42.9 per cent., respectively.

There can be little doubt that Harnack's muscarine aurichloride was choline aurichloride contaminated with muscarine aurichloride, which, as the physiological test indicates, is not easy to remove completely from choline aurichloride. His description of the aurichloride confirms this. Moreover, it seems unlikely that Harnack could have had the very large amounts of real muscarine aurichloride used in his analyses (the weight of his starting material, fresh or dry *A. muscaria*, is unfortunately not recorded), amounting to more than 8 grams. The present investigation has shown, by two different physiological methods of assay, that 25.5 kilos. of freshly-gathered *A. muscaria* contain only 0.4 gram of muscarine chloride, and Nothnagel, from many hundredweights of fresh material, could isolate only 0.5 gram of platinum salt. It is further to be noted that Harnack has recorded the activity of his pure gold salt, 1/20 to 1/30 mg. of muscarine chloride being required to stop the frog's heart in diastole, a value in agreement with that of

Schmiedeberg and Koppe, whose muscarine, according to Harnack's own showing, consisted of choline and muscarine with no attempt at their separation. The activity of the muscarine chloride now obtained pure is far in excess of this, only 1/500 mg. being required to stop the frog's heart in diastole, a value in agreement with Honda's estimate. If, then, as now seems certain, Harnack never had muscarine in even approximately pure condition, the edifice raised with so much labour on the basis of his analyses is deprived of its foundations.

Nothnagel's claim to the isolation of pure muscarine is more difficult to disprove. Neither he nor Hans Meyer gives any record of its physiological activity. The platinum value of his platinum salt, for which he unjustifiably assumes a content of  $2\text{H}_2\text{O}$ , a parallel assumption in the case of "synthetic muscarine" (choline nitrous ester) having led him into serious error, is not in agreement with his value for the gold salt. His description of the gold salt of muscarine, as small leaflets, agrees with that of the present author, but he apparently attaches no importance to the discrepancy between this description and that given by Harnack, according to whom choline and muscarine aurichlorides are identical in crystalline form.

Muscarine chloride has therefore a molecular or equivalent weight of the order of 210, whilst that of choline chloride is 137. Muscarine is not of the same order of simplicity as choline; there is no evidence for the accepted formula with one oxygen atom more than choline; it must be classed with alkaloidal bases of greater complexity, and there is no satisfactory evidence that it is a quaternary base. Fortunately, it appears to be very stable. It is not adsorbed by charcoal or kieselguhr, and its activity is unchanged after boiling with decinormal acid or alkali. The stability to alkali shows that it cannot be an ester of choline, some of which are intensely active. Arecoline, the methyl ester of *N*-methyltetrahydronicotinic acid, has a powerful muscarine-like action, but loses the whole of its activity after a few minutes' boiling with decinormal alkali.

I am indebted to Dr. H. H. Dale, F.R.S., for suggesting a simple means of following the distribution of the physiological activity during the many chemical operations necessary for the isolation of muscarine, by observing the effects on an isolated loop of rabbit's intestine. Without such control the isolation of muscarine would have been well-nigh impossible. I am also indebted to Dr. Dale and to Dr. J. H. Burn for carrying out the numerous physiological estimations required and for determining the limits of activity of pure muscarine chloride.

On an isolated loop of rabbit's intestine, muscarine chloride

produces a slightly sub-maximal contraction at a dilution of 1 in 67 millions, a dilution of 1 in 600 millions producing an appreciable effect. On the same organ, it is about seven times as active as arecoline and five times as active as acetylcholine.

On perfusion through the toad's heart in May, it caused stoppage in diastole at a dilution of 1 in 15 millions and a distinct inhibition at a dilution of 1 in 75 millions. It is also more active than acetylcholine on the toad's heart, 1 in 10 millions of acetylcholine failing to stop the same heart.

Both methods of assay agreed in assigning a content of 0.4 gram of muscarine chloride to the extract from 25.5 kilos. of fresh *A. muscaria*.

On the frog's heart in May, muscarine is somewhat less active than on the toad's heart. On perfusion, a dilution of 1 in 9.5 millions stopped the heart in diastole, and on subcutaneous injection into the lymph sac of the frog 0.0001 mg. per gram of frog was sufficient to stop the heart in diastole. Honda gives figures in almost exact agreement with these.

#### EXPERIMENTAL.

As a result of preliminary experiments in 1919 on the best method of preserving the physiological activity of *A. muscaria*, with a view to the eventual isolation of the active principle, it was found that the cleanest extract and one containing the maximum amount of muscarine was obtained by placing the fresh fungi into spirit without previous drying. At elevated temperatures, drying appeared to cause loss of activity, whilst drying in a vacuum at the ordinary temperature preserved the activity, but gave deeply coloured extracts.

Twenty-five and a half kilos. of fresh *A. muscaria*, collected in the birch woods in the neighbourhood of London in October, 1921, were put straightway into spirit, kept for a fortnight, and the spirit was decanted off and replaced by fresh spirit. The first and second extracts were combined and the fungi thoroughly pressed in a tincture press. The alcohol was removed under reduced pressure at a temperature below 50°, and the fat removed by ether extraction. Of the aqueous liquor, volume 2250 c.c., 2 c.c. were diluted to 200 c.c., heated at 100° to sterilise, and kept as a standard of reference for tracing the later distribution of the physiological activity due to muscarine. The main bulk of aqueous liquor was concentrated under reduced pressure, at a temperature below 50°, to a viscous syrup, and the latter thoroughly extracted with successive portions (about 5 litres in all) of absolute alcohol at 50°. The major portion of the muscarine was found by physiological assay to have passed

into the alcohol. Although the main bulk of syrup containing sugars and other inactive material had been removed, a considerable quantity of substances insoluble in absolute alcohol was contained in the alcoholic extract owing to the inevitable presence of water. After a long and tedious series of operations, in which the residues obtained on removing the alcohol and as much water as possible below  $50^{\circ}$  were thoroughly re-extracted with fresh absolute alcohol, also at temperatures below  $50^{\circ}$  (higher temperatures were found to yield empyreumatic substances which gave highly coloured solutions), and the residues therefrom were again and again submitted to the same treatment, so as to avoid loss of activity, a viscous syrup was finally obtained which was completely soluble in a large volume of absolute alcohol and when dissolved in 500 c.c. of water gave a bright yellow liquid with a green fluorescence (compare Harmsen, *Arch. Expt. Path. Pharm.*, 1903, **50**, 378).

The aqueous solution was treated with 837 c.c. of colloidal iron solution (5 per cent.  $\text{Fe}_2\text{O}_3$ ), the precipitate removed, and the filtrate, after concentration to 400 c.c., treated with a slight excess of basic lead acetate solution. After filtration and removal of the lead as sulphide, the filtrate was concentrated to a syrup, an extract made of the syrup with absolute alcohol, and finally an aqueous solution of the alcohol-soluble material. Again most of the muscarine present in the original extract was present in the purified solution.

The aqueous solution (125 c.c.) was treated with a litre of saturated mercuric chloride solution and kept below  $0^{\circ}$  over-night. The precipitate, mainly crystalline choline mercurichloride and about 50 grams in weight, was collected and extracted with successive portions of hot water, and filtered from amorphous matter, until the filtrate gave no reaction for chloridion. The mercury in the precipitate was removed as sulphide, and the filtrate therefrom, when tested physiologically, contained 14 per cent. of the original active material. The solution containing the main bulk of active material non-precipitable by aqueous mercuric chloride was freed from mercury as sulphide, from excess of hydrochloric acid as sodium chloride, and an alcoholic extract made. This was concentrated to 80 c.c., and 300 c.c. of saturated alcoholic mercuric chloride added together with 66 grams of finely powdered mercuric chloride. After keeping below  $0^{\circ}$  for a few days, the precipitate, mainly crystalline, was collected and worked up as described for the first aqueous mercuric chloride precipitation. The muscarine precipitated in this alcoholic mercuric chloride fraction was 34 per cent. of the original active material present.

As 52 per cent. of the muscarine was still unprecipitated by mercury salts, it appeared possible that the sodium acetate arising

from the process of neutralisation after removal of the lead from the basic lead acetate solution was partly responsible, especially as sodium acetate is known to inhibit the precipitation of choline by mercury salts (Smorodinzeff, *Z. physiol. Chem.*, 1912, **80**, 218). The solution after removal of mercury was therefore neutralised and freed from sodium chloride by extraction with absolute alcohol, the alcohol removed, and the residue dissolved in water (100 c.c.). A solution of colloidal iron was added as long as any further precipitation occurred, 280 c.c. being required in all. The filtrate was neutralised with sodium carbonate solution, and an extract made of the dried residue with absolute alcohol. The concentrated alcoholic solution, 25 c.c., was treated with 270 c.c. of hot saturated alcoholic mercuric chloride solution, and on keeping for several days below 0° there was a copious deposition of solid material. The liquor, moreover, set to an alcogel, which disappeared with slight rise of temperature. The precipitate was collected and was found to contain a further 15 per cent. of the original active material.

The filtrate was freed from mercury as sulphide and precipitated in 5 per cent. sulphuric acid solution (100 c.c.) with 120 c.c. of a 30 per cent. solution of phosphotungstic acid in 5 per cent. sulphuric acid solution. A small resinous deposit alone was obtained which contained the whole of the remaining active material, the filtrate being inactive. The precipitate was readily freed from phosphotungstic acid by treating with 100 c.c. of 5 per cent. sulphuric acid solution, and extraction of the free phosphotungstic acid by successive portions of an ether-amyl alcohol mixture (2:1) (compare Jacobs, *J. Biol. Chem.*, 1912, **12**, 429). The muscarine found in this precipitate was 17 per cent. of the original.

*The Phosphotungstic Acid Precipitate.*—This fraction, containing 17 per cent. of the muscarine, was somewhat coloured, weighed about 2.5 grams as chlorides or hydrochlorides, and was levorotatory. When treated in solution in absolute alcohol with hot saturated alcoholic mercuric chloride solution, the whole of the muscarine was precipitated, but on removal of mercury from the precipitate and filtrate and of excess of hydrochloric acid as sodium chloride, the relative weights of precipitate and non-precipitable were 0.5 and 1.8 grams and their rotations  $[\alpha]_D - 10^\circ$  and  $-18^\circ$ . Optical examination of other physiologically active fractions showed levorotation in all cases, but no parallelism between optical activity and physiological action.

*Fractionation of Choline and Muscarine as Tartrates.*—The liquors from the first two mercury precipitations containing the major portion of the choline and about 50 per cent. of the muscarine were combined, freed from excess of chloridion as sodium chloride,

and the chlorides of the bases present converted into carbonates by excess of silver carbonate. The carbonates were then converted into the *d*-hydrogen tartrates, and the choline isolated as choline *d*-hydrogen tartrate by concentration of the aqueous solution to a thin syrup at 50° and addition of a large volume of hot absolute alcohol in such a way that the syrup passed into solution and the dilution of the alcohol was about 95 per cent. Oily drops tended to separate on cooling, but on keeping over-night below 0° were replaced by crystalline choline *d*-hydrogen tartrate. By repeating the treatment on the mother-liquors a few times and recrystallising the choline *d*-hydrogen tartrate by the same technique, the major portion of the choline (15 grams of *d*-hydrogen tartrate) was isolated crystalline and the whole of the muscarine remained in the uncrystallisable syrup.

*Fractionation of the Gold Salts of Choline and Muscarine.*—Preliminary experiments with the uncrystallisable tartrate liquor containing the muscarine and some choline and other bases, and gold chloride, coupled with physiological control, showed that the muscarine tended to remain in the mother-liquors and to separate in the later oily fractions of gold salts, which slowly solidified. The presence of tartaric acid caused much reduction of gold and also inhibited crystallisation of the gold salts. In later fractionations, tartaric acid was first completely removed as normal sodium tartrate, which is insoluble in absolute alcohol.

The separation of choline and muscarine gold salts was effected as follows. The choline and muscarine chlorides and chlorides of other bases present were dissolved in 2 per cent. hydrochloric acid, treated with slight excess of 30 per cent. aqueous gold chloride solution, and concentrated to a suitable volume. The successive crops of choline aurichloride which separated were all accumulated and mixed so long as they remained wholly crystalline and composed of transparent crystals. Crude muscarine aurichloride as a rule tends to separate in quite easily distinguishable pale yellow nodules or aggregates. Even under the  $\frac{1}{4}$ -inch objective of a microscope no definite crystalline structure was visible. By picking out these warts or using other mechanical means of separation, about 0.5 gram was obtained. This was recrystallised from dilute acid with addition of a few drops of gold chloride solution and gave 0.29 gram, crystallising similarly, but with a slight improvement, as under the  $\frac{1}{4}$ -inch objective a few leaflets were visible. A second crystallisation gave a homogeneous crop of glistening, delicate leaflets of comparatively large size. The weight of pure muscarine aurichloride was 0.09 gram.

For analysis, the micro-analytical method with use of the

Kuhlmann micro-balance proved satisfactory. The method was first checked on choline aurichloride. Owing to the importance of the results they are given in detail.

For choline aurichloride :

Macro-analysis	0.1776	gave 0.0785 Au.	Au = 44.20.
Micro-analysis	0.01031	„ 0.00455 Au.	Au = 44.13.
	0.01231	„ 0.00545 Au.	Au = 44.28.
$C_5H_{14}ONAuCl_3$ requires Au = 44.49 per cent.			

For muscarine aurichloride :

0.01080,	dried at 95–100°,	lost 0.00002.
0.01078,	dry,	gave 0.00416 Au. Au = 38.6 per cent.

From the mother-liquors, after many more fractionations, a further 0.034 gram of muscarine aurichloride was isolated, crystallising as before in homogeneous, delicate leaflets. On micro-analysis, 0.01565 gave 0.00591 Au, whence Au = 37.8, a value of the same order as that obtained with the previous preparation. The mean of these gives an equivalent or molecular weight of muscarine chloride of the order of 210.

*Comparison of Choline and Muscarine.*—With phosphotungstic acid, both give a voluminous, white precipitate. With Mayer's reagent (potassium mercuric iodide), choline gives a crystalline precipitate, whilst muscarine gives an oily salt soluble in excess of the reagent. With a very concentrated solution of mercuric iodide in potassium iodide, choline gives an oil which rapidly crystallises in needles or octahedra, soluble in excess of the precipitant but reprecipitated by dilute sulphuric acid; muscarine, however, gives yellow, oily drops very readily soluble in excess of the reagent and reprecipitated as an oil by dilute acid. With platinum chloride in aqueous solution, choline gives on concentration prisms or rhombs, whereas muscarine gives on concentration octahedra, cubes, and tetrahedra. Unlike choline, muscarine gives no precipitate with aqueous mercuric chloride. With iodine in potassium iodide, both give dark-coloured, oily drops, and with bromine water a finely divided precipitate which rapidly disappears. From a moderately concentrated muscarine chloride solution, solid sodium hydroxide sets free a pale yellow oil which, apparently, is not taken up by chloroform. On heating, a basic vapour with an odour of decaying fish was evolved, but not a pure trimethylamine odour.

*Other Constituents of A. muscaria.*—On removal of the ether from the ethereal solution of the fat from *A. muscaria*, a crystalline substance separated at the boundary of the fat and separated water phase. The solid was collected, weighed 0.25 gram, melted at 159°, and gave the phytosterol colour reactions. The crude

material, dried at  $100^{\circ}$ , lost 4.5 per cent. and gave  $[\alpha]_D - 103^{\circ}$  in chloroform ( $c = 0.48$ ). It was acetylated, and then melted, after crystallisation from alcohol, from which it separated in glistening leaflets of indefinite shape, at  $170-172^{\circ}$ . On hydrolysis and crystallisation from alcohol, it separated in glistening leaflets and melted, when dried at  $90^{\circ}$ , at  $158-159^{\circ}$ . The amount of material for analysis was only 0.089 gram. It lost 4.5 per cent. on drying and then gave  $C = 83.3$ ;  $H = 11.0$ , whereas  $C_{26}H_{40}O$  requires  $C = 84.7$ ;  $H = 10.9$ ;  $C_{26}H_{44}O$  requires  $C = 83.8$ ;  $H = 11.9$  per cent.;  $C_{20}H_{30}O \cdot H_2O$  requires  $H_2O = 4.7$  per cent. The substance agrees well with Tanret's ergosterol from ergot and amplifies the observations of Zellner (*Monatsh.*, 1905, **26**, 727) on ergosterol in *A. muscaria*. A comparison was made of the colour reactions of this ergosterol and its acetyl derivative with those of pure cholesterol and its acetyl derivatives by the Hesse-Salkowski, Liebermann, and Denigès reactions. Ergosterol and its acetyl derivative were in each case more reactive than cholesterol and gave different colour reactions, and moreover, when heated at  $95-100^{\circ}$ , the solids became coloured. These observations are probably traceable to the increased number of unsaturated linkings in ergosterol (McLean and Thomas, *Biochem. J.*, **14**, 1920, 491).

During the extraction of the alcohol-soluble material from the main bulk of syrupy material from *A. muscaria* by hot alcohol, syrupy deposits were obtained, on cooling, which occasionally contained crystalline material. Three substances were readily isolated pure, potassium chloride, *L*-leucine, and mannitol. *L*-Leucine gave  $[\alpha]_D - 8.1^{\circ}$  in water ( $c = 0.5$ ), volatilised partly at  $295^{\circ}$ , and decomposed between  $298^{\circ}$  and  $305^{\circ}$  according to the rate of heating (Found:  $N = 10.6$ .  $C_6H_{13}O_2N$  requires  $N = 10.7$  per cent.). *L*-Leucine has previously been recorded as occurring in this fungus by Ludwig (*Jahresber. Chem.*, 1862, 516). Mannitol has not apparently been recorded as occurring in *A. muscaria*. It was obtained in quantity and identified by comparison with an authentic specimen. In the presence of borax its aqueous solution showed a dextrorotation, proving the mannitol present to be levorotatory. All attempts to isolate trehalose, the parent substance of mannitol in fungi and known to occur in *A. muscaria*, were fruitless.

Fumaric acid was found in the basic lead acetate precipitate, confirming a similar observation by Zellner. Its isolation in a clean condition is best effected by extraction with ether.

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CCXI.—The  $\beta$ -Chlorovinylarsines.

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

ACETYLENE is absorbed by arsenic trichloride in presence of aluminium chloride, and from the product, after treatment with water, three substances of novel types may be isolated, namely,  $\beta$ -chlorovinylchloroarsine,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsCl}_2$ ,  $\beta\beta'$ -dichlorodivinylchloroarsine,  $(\text{CHCl}\cdot\text{CH})_2\text{AsCl}$ , and  $\beta\beta'\beta''$ -trichlorotrivinylarsine,  $(\text{CHCl}\cdot\text{CH})_3\text{As}$ . A brief description of the reaction involved and of the properties of the products has been given by Green and Price (T., 1921, 119, 448), and the results of a fuller examination of the chlorovinylarsines are recorded in the present paper.

The mixture of the three above-named arsines, prepared as described by Green and Price, was carefully fractionated with the aid of a long glass column packed with short sections of glass tubing in imitation of the Raschig ring dephlegmator. The pure components thus separated have the following boiling points:

$\beta$ -Chlorovinylchloroarsine:  $76-77^\circ/12.5$  mm. and  $82^\circ/16.5$  mm.

$\beta\beta'$ -Dichlorodivinylchloroarsine:  $108-109^\circ/10.5$  mm.,  $116-117^\circ/15$  mm., and  $120-121^\circ/17$  mm.

$\beta\beta'\beta''$ -Trichlorotrivinylarsine:  $139-140^\circ/13$  mm. and  $144^\circ/16$  mm. This substance crystallises on cooling in long, white needles which melt at  $23^\circ$ .

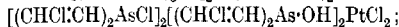
These three arsines are converted by oxidation into the corresponding quinquevalent arsenic compounds. The  $\beta$ -chlorovinylarsinic acid,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsO}(\text{OH})_2$ , obtained from the primary dichloroarsine, gives a mono-ammonium salt; the  $\beta\beta'$ -dichlorodivinylarsinic acid,  $(\text{CHCl}\cdot\text{CH})_2\text{AsO}(\text{OH})$ , formed from the secondary chloroarsine, gives a well-defined nitrate together with stable metallic salts, whilst the oxidation product,  $(\text{CHCl}\cdot\text{CH})_3\text{AsO}$ , of the tertiary arsine yields a crystalline nitrate, but does not behave as an acid. The latter oxide corresponds with the arsine dibromide,  $(\text{CHCl}\cdot\text{CH})_3\text{AsBr}_2$ , and the methiodide,  $(\text{CHCl}\cdot\text{CH})_3\text{As}(\text{CH}_3)\text{I}$ , described below.

The tertiary arsine condenses with chloramine T, yielding a product of the constitution  $(\text{CHCl}\cdot\text{CH})_3\text{As}\cdot\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$ ; this compound is of a novel type, containing the grouping  $\text{>As}\cdot\text{N}$ , and may be termed an "arsylimine" from its analogy to the sulphimines, containing the group  $\text{=S}\cdot\text{N}$ —, which we have recently described (this vol., p. 1052). The tenacity with which the arsilimine retains one molecular proportion of water arouses the suspicion that it may contain the saturated grouping,  $\text{>As}(\text{OH})\cdot\text{NH}$ —.

The behaviour of the tertiary arsine towards platonic, palladous,

and auric chlorides is of interest. Cahours and Gal (*Compt. rend.*, 1870, **70**, 897, 1380; **71**, 208) found that triethylphosphine reacts with platinic chloride, yielding two isomeric platinochlorides, of the composition  $(\text{Et}_3\text{P})_2\text{PtCl}_2$ , both of which combine with more of the phosphine giving the platnichloride,  $(\text{Et}_3\text{P})_4\text{PtCl}_2$ ; they obtained an analogous set of compounds with triethylarsine and platinic chloride and showed that triethylarsine yields the compounds  $(\text{Et}_3\text{As})_2\text{PdCl}_2$  and  $\text{Et}_3\text{AsAuCl}$  with palladous and auric chlorides, respectively.

We find that  $\beta\beta'\beta''$ -trichlorotrivinylarsine behaves like triethylarsine towards palladous and auric chlorides, yielding the substances  $[(\text{CHCl}\cdot\text{CH})_3\text{As}]_2\text{PdCl}_2$  and  $(\text{CHCl}\cdot\text{CH})_3\text{AsAuCl}$ , but that its behaviour towards platinic chloride is different. We have obtained two compounds which analysis shows to correspond with the formulæ  $[(\text{CHCl}\cdot\text{CH})_3\text{As}]_2\text{Pt}(\text{CH}\cdot\text{CHCl})_2$  and



if these constitutional formulæ are correct, and this we cannot yet assert, the substances correspond in type of constitution with the triethylphosphine and triethylarsine platino- and platini-chlorides of Cahours and Gal.

#### EXPERIMENTAL.

$\beta$ -Chlorovinylarsinic Acid,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsO}(\text{OH})_2$ .— $\beta$ -Chlorovinyl-dichloroarsine is vigorously oxidised when warmed with an equal volume of concentrated nitric acid; the oxidation sets in spontaneously in the cold, and the resulting solution, when chilled and scratched, deposits  $\beta$ -chlorovinylarsinic acid as a mass of colourless crystals. The acid crystallises from a mixture of acetone and carbon tetrachloride in long needles melting at  $130^\circ$  (Found: Cl = 19.1.  $\text{C}_2\text{H}_4\text{O}_3\text{ClAs}$  requires Cl = 19.0 per cent.).

When the acid is heated in a vacuum at  $110$ – $115^\circ$ , it loses one molecular proportion of water, giving the corresponding anhydride,  $\beta$ -chlorovinylarsinic oxide,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsO}_2$  (loss found = 9.68.  $\text{H}_2\text{O}$  requires 9.66 per cent.). The anhydride forms a fine, white, hygroscopic powder and decomposes violently at  $242^\circ$  (Found: Cl = 20.7.  $\text{C}_2\text{H}_2\text{O}_2\text{ClAs}$  requires Cl = 21.0 per cent.). All attempts to recrystallise it resulted in the production of the original acid.

The mono-ammonium salt,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsO}(\text{OH})\cdot\text{O}\cdot\text{NH}_4$ , crystallises on evaporating an ammoniacal aqueous solution of the acid and is obtained in six-sided plates or in long needles; it melts at  $163^\circ$  with decomposition (Found: Cl = 17.4; N = 7.0.  $\text{C}_2\text{H}_7\text{O}_3\text{NClAs}$  requires Cl = 17.4; N = 6.9 per cent.).

We were unable to prepare  $\beta$ -chlorovinylarsenious oxide,  $\text{CHCl}\cdot\text{CH}\cdot\text{AsO}$ , by hydrolysing the corresponding chloride with

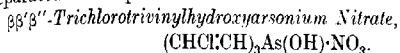
potassium carbonate or dilute sodium hydroxide in the cold, only arsenious acid and acetylene being obtained, as indicated by the experiments of Green and Price. On treating the chloride in carbon tetrachloride solution with hydrogen sulphide, hydrogen chloride is evolved and a viscous liquid deposited; the latter is purified by solution in carbon disulphide and evaporating, when a pale-yellow, viscid liquid with a strong garlic-like odour results. This substance solidifies to a hard resin on strong cooling, but could not be induced to crystallise; analysis showed it to be the impure  $\beta$ -chlorovinylarsenious sulphide,  $\text{CHCl:CH}\cdot\text{AsS}$ , but no satisfactory method for purifying it was found.

$\beta\beta'$ -Dichlorodivinylarsinic Acid,  $(\text{CHCl:CH})_2\text{AsO}\cdot\text{OH}$ .—Green and Price obtained a crystalline oxidation product, melting at  $97^\circ$ , by the action of nitric acid on  $\beta\beta'$ -dichlorodivinylchloroarsine; the preparation was repeated, the solid product being recrystallised from chloroform. The colourless, needle-shaped crystals thus obtained melt at  $99^\circ$  and consist of  $\beta\beta'$ -dichlorodivinylarsinic acid nitrate,  $(\text{CHCl:CH})_2\text{AsO}\cdot\text{OH}\cdot\text{HNO}_3$  (Found: Cl = 24.3; N = 4.7.  $\text{C}_4\text{H}_5\text{O}_5\text{NCl}_2\text{As}$  requires Cl = 24.1; N = 4.8 per cent.).

This salt seems to resist hydrolytic dissociation, but is decomposed when dissolved in water, with the aid of alcohol, and treated with sufficient standard sodium hydroxide solution to neutralise the nitric acid present; on extracting the aqueous solution with chloroform and evaporating the extract, the free  $\beta\beta'$ -dichlorodivinylarsinic acid,  $(\text{CHCl:CH})_2\text{AsO}\cdot\text{OH}$ , remains as a crystalline mass. The acid crystallises in colourless needles from carbon tetrachloride containing a little benzene, and melts at  $120^\circ$  (Found: Cl = 30.8.  $\text{C}_4\text{H}_5\text{O}_2\text{Cl}_2\text{As}$  requires Cl = 30.7 per cent.). The ammonium salt cannot be prepared in aqueous solution, but on evaporating an aqueous alcoholic solution of the acid with the equivalent quantity of caustic potash solution, the potassium salt,  $(\text{CHCl:CH})_2\text{AsO}\cdot\text{OK}\cdot 4\text{H}_2\text{O}$ , crystallises in colourless plates (Found: K = 11.4; Cl = 20.8.  $\text{C}_4\text{H}_{12}\text{O}_6\text{Cl}_2\text{AsK}$  requires K = 11.5; Cl = 20.8 per cent.). The crystals melt at  $49^\circ$  and (when kept in a vacuum over phosphoric oxide for several days) yield the anhydrous salt as a white, hygroscopic powder melting at  $158^\circ$  with decomposition (Found: K = 14.7; Cl = 26.1.  $\text{C}_4\text{H}_4\text{O}_2\text{Cl}_2\text{AsK}$  requires K = 14.5; Cl = 26.4 per cent.).

The sodium salt,  $(\text{CHCl:CH})_2\text{AsO}\cdot\text{ONa}\cdot 4\text{H}_2\text{O}$ , prepared in a similar manner, forms small, colourless plates melting at  $70^\circ$  (Found: Na = 7.1.  $\text{C}_4\text{H}_{12}\text{O}_6\text{Cl}_2\text{AsNa}$  requires Na = 7.1 per cent.). Dr. H. H. Dale, F.R.S., of the National Institute for Medical Research, reports that this substance has no effect of any importance on *Trypanosoma equiperdum* infection in mice.

$\beta\beta'$ -Dichlorodivinychloroarsine yields a clear solution when boiled in aqueous solution with the equivalent quantity of chloramine T; only  $\beta\beta'$ -dichlorodivinyarsinic acid and *p*-toluenesulphonamide could be isolated from the solution. The oxide corresponding with the chloroarsine could not be prepared by treating the latter with the calculated quantity of caustic alkali; in light petroleum solution, the chloroarsine yields a granular, orange-red precipitate on addition of one molecular proportion of bromine, but this perbromide gives off hydrogen bromide when separated and exposed to the air.



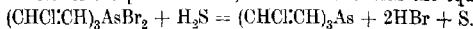
— $\beta\beta'\beta''$ -Trichlorotrivinylarsine is attacked violently by nitric acid and it is desirable to oxidise it in quantities of not more than 2 grams by cautious warming with an equal volume of concentrated nitric acid in a capacious flask; a mass of colourless crystals is deposited on cooling, and this product, when crystallised from a little chloroform, separates in small needles melting at  $103^\circ$  (Found: Cl = 31.3; N = 4.1.  $\text{C}_6\text{H}_7\text{O}_4\text{NCl}_3\text{As}$  requires Cl = 31.4; N = 4.1 per cent.). When the hydroxy-nitrate is treated in aqueous solution with an equivalent of caustic soda, the solution extracted with chloroform, and the chloroform extract evaporated, a crystalline residue is obtained; on crystallising this from benzene containing a little carbon tetrachloride,  $\beta\beta'\beta''$ -trichlorotrivinylarsenic oxide,  $(\text{CHClCH})_3\text{AsO}$ , separates in long, colourless needles or in small plates which melt with decomposition at  $154^\circ$  (Found: Cl = 38.7.  $\text{C}_6\text{H}_6\text{OCl}_3\text{As}$  requires Cl = 38.6 per cent.).

$\beta\beta'\beta''$ -Trichlorotrivinylarsine dibromide,  $(\text{CHClCH})_3\text{AsBr}_2$ , separates in colourless needles, which melt at  $107^\circ$ , when  $\beta\beta'\beta''$ -trichlorotrivinylarsine is cautiously treated in a freezing mixture with bromine (1 mol.), both in light petroleum solution. The substance is conveniently analysed by weighing the silver bromide precipitated on adding silver nitrate to its solution acidified with nitric acid (Found: Br = 38.4.  $\text{C}_6\text{H}_6\text{Cl}_3\text{Br}_2\text{As}$  requires Br = 38.1 per cent.). The dibromide may be recrystallised from boiling light petroleum, but the needle-shaped crystals which separate are followed by smaller crystals of some other product which melt at about  $119^\circ$ . On hydrolysing the dibromide by treatment with the calculated quantity of sodium hydroxide solution and extracting the clear solution with chloroform, the corresponding arsenic oxide melting at  $154^\circ$  is obtained by evaporating the chloroform extract.

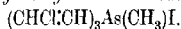
On adding bromine (3 mols.) to the trichlorotrivinylarsine, both in cold light petroleum solution, a deep red precipitate is formed;

this substance seems to be stable in a vacuum, but becomes white when preserved for several days in a bottle.

$\beta\beta'$ -Trichlorotrivinylarsine sulphide,  $(\text{CHCl}\cdot\text{CH})_3\text{AsS}$ , could not be prepared by heating the arsine under reflux with sulphur in benzene or ether solution or by heating it with sulphur at  $100^\circ$ . Hydrogen sulphide acts on the dibromide in chloroform solution with evolution of hydrogen bromide, deposition of sulphur, and regeneration of the parent arsine, in accordance with the equation

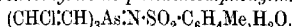


$\beta\beta'\beta''$ -Trichlorotrivinylmethylarsonium Iodide,



—On heating the arsine with an equimolecular proportion of methyl iodide for twenty-seven hours at  $100^\circ$  in a sealed tube, the mixture solidifies almost completely to a mass of needle-shaped crystals; after washing the solid with petroleum and recrystallising it from alcohol, the methylarsonium iodide is obtained in lustrous, colourless needles melting at  $209^\circ$ . The iodide is analysed by acidifying its aqueous solution with nitric acid and collecting the silver iodide which is precipitated in the cold on addition of silver nitrate solution (Found:  $\text{I} = 31.4$ .  $\text{C}_7\text{H}_9\text{Cl}_3\text{IAs}$  requires  $\text{I} = 31.6$  per cent.).

$\beta\beta'\beta''$ -Trichlorotrivinylarsine-*p*-toluenesulphonylimine,



—A solution of the tertiary arsine is boiled in acetone solution with chloramine T (1 mol.) for twenty minutes, filtered, and the filtrate evaporated to dryness; the crystalline residue is washed with water and boiled with ether to extract sodium chloride and toluene-sulphonamide, and then recrystallised from benzene. The arsyl imine is thus obtained in colourless plates melting at  $124^\circ$  (Found:  $\text{C} = 34.7$ ;  $\text{H} = 3.4$ ;  $\text{N} = 3.1$ ;  $\text{Cl} = 23.8$ .  $\text{C}_{13}\text{H}_{15}\text{O}_3\text{NCl}_3\text{SAs}$  requires  $\text{C} = 34.9$ ;  $\text{H} = 3.4$ ;  $\text{N} = 3.1$ ;  $\text{Cl} = 23.8$  per cent.). When the powdered solid is added to hot benzene containing a fragment of calcium carbide, no evolution of acetylene occurs; it is therefore possible that the compound contains the grouping  $\text{NH}\cdot\text{As}(\text{OH})$  and that the molecule of water, the presence of which is shown by the analyses, is not present as solvent of crystallisation.

*Platinum Bis- $\beta$ -chlorovinylbis- $\beta\beta'\beta''$ -trichlorotrivinylarsine*,  $[(\text{CHCl}\cdot\text{CH})_3\text{As}]_2\text{Pt}(\text{CH}\cdot\text{CHCl})_2$ .—When an aqueous solution of chloroplatinic acid, diluted with alcohol, is added to an alcoholic solution of the tertiary arsine, long, very pale yellow needles separate, followed later by short, lemon-yellow prisms; the mixture of crystals is removed and vigorously agitated with a little benzene, by which means a residue consisting only of the needles is obtained. This substance crystallises from alcohol in very pale yellow, almost white, needles and from benzene in pale yellow

plates; it melts at  $198^\circ$  with decomposition (Found: C = 22.9; H = 1.9; Cl = 33.8; Pt = 23.0.  $C_{16}H_{18}Cl_8As_2Pt$  requires C = 22.9; H = 1.9; Cl = 33.9; Pt = 23.3 per cent.).

*Bis- $\beta\beta'$ -dichlorodivinylchloroarsinebis- $\beta\beta'$ -dichlorodivinylhydroxyarsine Platinichloride*,  $[(CHCl:CH)_2AsCl]_2[(CHCl:CH)_2As\cdot OH]_2PtCl_2$ .

—The crystalline mixture obtained above is agitated with dry ether until the latter is saturated, and the ethereal extract allowed to evaporate spontaneously; the pale yellow needles separate on the sides of the beaker and a crust of the lemon-yellow plates is formed on the bottom. The latter is further purified by crystallisation from alcohol and melts with decomposition at  $196^\circ$ ; it is formed in quantity only in presence of a decided excess of the tertiary arsine (Found: C = 16.5; H = 1.4; Cl = 36.6.  $C_{16}H_{18}O_2Cl_{12}As_4Pt$  requires C = 16.5; H = 1.6; Cl = 36.6 per cent.).

*Bis- $\beta\beta'\beta''$ -trichlorotrivinylarsine Palladichloride*,  
 $[(CHCl:CH)_3As]_2PdCl_2$ .

—An alcoholic solution of palladous chloride is added to a cooled alcoholic solution of the tertiary arsine; long, yellowish-brown needles begin to form within a few seconds and are ultimately separated and washed with a little ether. The substance melts with decomposition at  $196^\circ$  and is soluble in ether and acetone (Found: Cl = 40.5; Pd = 15.5.  $C_{12}H_{12}Cl_6As_2Pd$  requires Cl = 40.7; Pd = 15.3 per cent.). The formation of this characteristic compound furnishes a ready means for detecting the presence of the tertiary arsine.

*$\beta\beta'\beta''$ -Trichlorotrivinylarsine Aurichloride*,  $(CHCl:CH)_3AsAuCl$ .—On adding an alcoholic solution of potassium aurichloride to a cooled alcoholic solution of the tertiary arsine, the mixture rapidly becomes colourless and then slowly deposits small, heavy, white crystals. After washing and drying, the substance melts at  $123^\circ$  with decomposition (Found: Au = 40.0.  $C_6H_6Cl_3AsAu$  requires Au = 40.1 per cent.). On exposing the colourless crystals to light for several days, they gradually acquire a purplish-grey colour.

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CCXII.—*Catalysis of Hydrogen Peroxide by Finely Divided Platinum. The Influence of Inhibitants.*

By EDWARD BRADFORD MAXTED.

IN previous communications (T., 1920, 117, 1501; 1921, 119, 225, 1280), it has been shown that the activity of a catalyst for the hydrogenation of an ethylenic linking, in the presence of varying concentrations of certain inhibitants, is a linear function of the concentration of the poison. In certain cases, the main linear portion of this poisoning curve persists until more than 90 per cent. of the catalytic activity has been suppressed, whilst with further additions of the inhibitant the activity of the catalyst falls off far less steeply. It appeared desirable to test the applicability of a linear poisoning law to other types of reaction, and with this in view the catalysis of hydrogen peroxide with finely divided platinum has been chosen for study. Bredig, Ikeda, and Reinders (*Z. physikal. Chem.*, 1901, 37, 1, 323; "Anorganische Fermente," Leipzig, 1901) have examined this reaction in detail, and a study of their results with iodine, bromine, hydroxylamine, and hydrochloric acid as inhibitants shows that these are not incompatible with an initially linear poisoning law. The results of Bredig and his collaborators with cyanogen iodide are apparently inconsistent with a linear graph, whilst those obtained for other inhibitants are inadequate for the present purpose; moreover, in any case, the number of points in positions suitable for testing this linear relationship is not large, especially in view of the relatively high experimental error.

In the further experiments which have accordingly been made, the platinum catalyst was used in a non-colloidal condition, in order to avoid complications due to coagulation. Further, poisons such as hydrogen cyanide or carbon monoxide, which, by oxidation or otherwise, are changed into products of different toxicity, were avoided, and those actually used—mercuric chloride, mercuric nitrate, and lead acetate—can be regarded as remaining constant in concentration throughout an experiment. The results obtained with these inhibitants show that, for a wide range, the activity of the catalyst is a linear function of the concentration of the poison. With still higher concentrations of the poison, the extinction of activity is far less abrupt.

EXPERIMENTAL.

In order to prepare an aqueous suspension of finely divided platinum of constant activity, an approximately  $N/20$ -solution of

platinic chloride was reduced by means of formaldehyde according to Loew's method (*Ber.*, 1890, **23**, 289), and the precipitated metal, after careful washing by decantation, was made into a suspension with water such that 1 c.c. of the liquid, after agitation, corresponded with 0.2 mg. of platinum. This suspension, after agitation, was sufficiently uniform in concentration to be subdivided by means of a pipette, and the weight of platinum removed in this way was sufficiently constant to cause a close agreement between duplicate experiments (see below). The solutions of mercuric chloride, lead acetate, and mercuric nitrate employed contained 0.1 mg. of mercury, 0.0835 mg. of lead, and 0.05 mg. of mercury per c.c., respectively. The stock solution of hydrogen peroxide used for the first series of measurements contained approximately 30 grams of hydrogen peroxide per litre, whilst for the second and third series a second solution, containing 22.6 grams per litre, was taken. These were prepared by diluting two samples of commercially pure hydrogen peroxide, it having been previously ascertained that the degree of freedom of these samples from inhibitors was such that the velocity coefficient during individual experiments remained sufficiently constant for the quantitative comparison of the values of this figure in the presence of varying concentrations of the inhibitor. The activity of the catalyst was, as before, assumed to be proportional to the effect produced by it, that is to say, to the initial magnitude of the velocity coefficient produced under similar conditions.

*Series 1. Inhibition by Mercury as Mercuric Chloride.*

In order to carry out a measurement, 1 c.c. of platinum catalyst, corresponding with 0.2 mg. of platinum, followed by sufficient water to amount, together with that subsequently introduced with the inhibitor, to 3.5 c.c. in all, was placed in a 25 c.c. shaking-vessel. The desired quantity of mercuric chloride was now added, and the mixture kept for thirty minutes at 20°. This period of incubation is, as Bredig also observed, necessary for the attainment of constant results. Little or no difference was, however, noticed between the activity of a catalyst which had been subjected to the action of the poison for thirty minutes and for twelve hours respectively; and, accordingly, the poisoning action may be regarded as complete after the period of incubation employed. Eight c.c. of stock hydrogen peroxide, containing 30 grams of hydrogen peroxide per litre, and previously brought to 20°, were now added. The shaking-vessel was connected without delay with a measuring apparatus of the type previously employed (*Trans. Faraday Soc.*, 1917, **13**, 36), and shaken at a uniform high speed,



in order to avoid supersaturation, in a thermostat at  $20^{\circ}$ , the rate of decomposition being measured by the oxygen evolved. In this series, the shaker was started fifteen seconds prior to the beginning of the experiment, in order to ensure a uniform condition of agitation; and the oxygen evolved during this short preliminary period was subtracted from the original oxygen value of the peroxide taken, in order to determine  $a$ , the concentration of peroxide at the beginning of the experiment proper. For the object in view, namely, the determination of the initial activity of the catalyst in the presence of various known quantities of the inhibitant, the speed of the reaction during the first few minutes is of special interest. With the materials and inhibitants employed in the present work, the decomposition proceeded in every case approximately according to the unimolecular reaction law. A slight decrease in the activity of the catalyst took place, however, as the reaction proceeded, but the initial activity could easily be obtained by extrapolating the values of  $k$  for that corresponding with  $t = 0$ , and, in any case, the variation in  $k$  during the period of observation did not usually exceed 10 per cent. of its original value.

In all, seventeen measurements were carried out in the first series of experiments, using mercuric chloride as the inhibitant. Details of three typical individual decomposition experiments are given below, and serve to indicate the nature of the results obtained. The results of the remaining experiments, which were very similar, are tabulated in less detail later. In the following tables, the initial concentration,  $a$ , also  $a - x$ , the concentration of hydrogen peroxide after  $t$  minutes, are expressed in gram-molecules per litre; and, in calculating  $k$ , logarithms to base 10 have been used, since relative values only are required. The weights of mercury given refer to the actual mercury content of the system.

TABLE I.

Hg = 0.		
$t$ .	$a - x$ .	$k$ .
0	0.512	—
1	0.457	0.049
2	0.411	0.048
3	0.370	0.047
4	0.334	0.047
5	0.301	0.046

TABLE II.

Hg = 0.05 mg.		
$t$ .	$a - x$ .	$k$ .
0	0.481	—
1	0.447	0.032
2	0.416	0.0315
3	0.387	0.0315
4	0.361	0.031
5	0.339	0.0305

TABLE III.

Hg = 0.1 mg.		
$t$ .	$a - x$ .	$k$ .
0	0.571	—
1	0.552	0.015
2	0.533	0.015
3	0.516	0.0145
4	0.500	0.0145
5	0.487	0.014

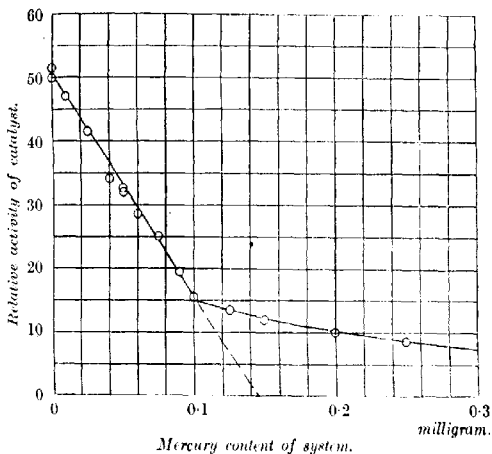
The initial values of  $k$ , corresponding with each concentration of inhibitant studied, were obtained from the individual results by extrapolation for  $t = 0$ ; and, on tabulating the series of values, it was noted that the activity of the catalyst decreases at first

regularly and uniformly with corresponding additions to the poison content of the system, until a later stage is reached, during which the influence of additional increments of poison is far less marked. The values of  $k_0$  for the seventeen measurements made with various concentrations of inhibitor have been collected in Table IV.

TABLE IV.

Mercury content of system in mg.	Relative initial activity of catalyst ( $k_0 \times 10^3$ ).	Mercury content of system in mg.	Relative initial activity of catalyst ( $k_0 \times 10^3$ ).	Mercury content of system in mg.	Relative initial activity of catalyst ( $k_0 \times 10^3$ ).
0	50	0.05	32	0.125	13.5
0	51.5	0.06	28.5	0.15	12
0.01	47	0.075	25	0.2	10
0.025	41.5	0.09	19.5	0.25	8.5
0.04	33.5	0.1	15.5	0.5	0.5
0.05	32.5	0.125	13.5		

FIG. 1.



The linear nature of the main portion of the poisoning curve is best seen by plotting graphically the catalytic activity of the platinum against the poison content. Reference to Fig. 1 shows that this curve is of the same type as that previously found for the inhibition of the activity of catalysts for the hydrogenation of an ethylenic linking. The deviation from the linear course occurs at a stage at which slightly less than three-quarters of the original activity has been suppressed.

In the above measurements with mercuric chloride, it is probable that the chlorine ion, in addition to the mercury, contributes to a certain extent towards the total inhibitive action observed; but, since the salt may, in the extremely dilute solutions employed, be regarded as completely dissociated throughout, and since, in any case, the addition of a given increment of mercury involves the addition of an equivalent quantity of chlorine ions, the possibility of additional poisoning by the acidic ion will not affect the applicability of the results to the end in view, namely, as a test of the extension of the linear poisoning relationship to the decomposition of hydrogen peroxide.

*Series II. Inhibition by Mercury as Mercuric Nitrate.*

A number of determinations were also made in the presence of mercuric nitrate, prepared by dissolving mercury in nitric acid, and acidified with a drop of nitric acid in order to prevent turbidity. The experiments were carried out under similar conditions to those previously employed, save that 0.3 mg. of a further preparation of platinum and 10 c.c. of the second stock solution of hydrogen peroxide were taken for each measurement. The values of  $k_0$ , corresponding with the weights of inhibitor stated, are given in Table V.

TABLE V.

Mercury as Nitrate. Pt = 0.3 mg.

Mercury content of system in mg.	Relative activity of catalyst ( $k_0$ ).	Mercury content of system in mg.	Relative activity of catalyst ( $k_0$ ).
0	0.034	0.03	0.013
0	0.035	0.04	0.0105
0.01	0.029	0.05	0.011
0.015	0.0235	0.06	0.009
0.02	0.021	0.08	0.008

The curve is of an initially linear type, similar to that previously obtained with mercury in the form of chloride.

*Series III. Inhibition by Lead as Lead Acetate.*

Two aqueous solutions of lead acetate, containing respectively 0.0835 mg. and 0.448 mg. of lead per c.c., were taken as the inhibitor, the latter solution being used for measurements in the presence of relatively large proportions of the poison. The other components of the reacting system and the experimental conditions were similar to those used for mercuric nitrate, save that the shaking apparatus was started at the actual commencement of the experiment, in place of fifteen seconds previously, so that the initial concentration of peroxide for the point  $t = 0$  is here uniform.

The variation in the activity of the catalyst, measured as before by the initial value of  $k$ , with varying concentrations of poison, is given in Table VI.

TABLE VI.

Lead content of system in mg.	Relative initial activity of catalyst ( $k_0 \times 10^3$ ).	Lead content of system in mg.	Relative initial activity of catalyst ( $k_0 \times 10^3$ ).
0	34	0.0835	17.5
0.0167	30	0.125	13.5
0.0224	28	0.224	11
0.0334	27	0.56	10
0.067	21	0.67	9.5
0.075	18		

The curve obtained by plotting the above results graphically is linear for a large portion of its length.

In addition to the above measurements, a series was begun with arsenic in the form of sodium arsenate, but the toxic properties of this substance, in contrast to its effect in catalytic hydrogenation (in which arsine is probably the active inhibitor), were found to be relatively low, an effect which was also noticed by Bredig.

In view of the probability that catalyst poisoning of the type studied is due to a preferential adsorption of the inhibitor on the surface lattice of the catalyst, an investigation of the degree of this adsorption is of considerable interest. From preliminary experiments, it would appear that dilute solutions of inhibitors such as catalytically poisonous metals are strongly adsorbed by platinum catalysts; but the adsorption is incomplete, except probably in the presence of relatively large concentrations of catalyst. Further work on the form of the adsorption curve is proceeding.

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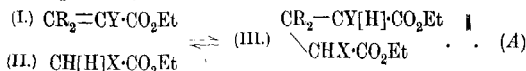
[Received, July 11th, 1922.]

CCXIII.—*Ring-chain Tautomerism. Part III. The Occurrence of Tautomerism of the Three-carbon (Glutaconic) Type between a Homocyclic Compound and its Unsaturated Open-chain Isomeride.*

By CHRISTOPHER KELK INGOLD, EDWARD ARTHUR PERREN, and  
JOCELYN FIELD THORPE.

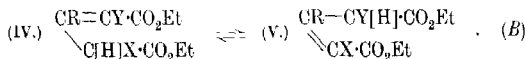
It has recently been pointed out (Ingold and Perren, T., 1921, 119, 1582; Ingold and Powell, *ibid.*, p. 1976) that the condensation, usually termed Michael's reaction, between  $\alpha\beta$ -unsaturated esters

and compounds, such as ethyl cyanoacetate, which contain a reactive hydrogen atom (marked [H] in the formulæ below) is a reversible process, the condensation product (III) undergoing fission into components (I and II) under the conditions of its formation :



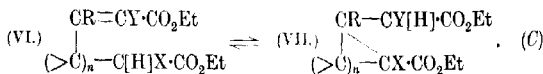
In general, therefore, the result is a balanced action; for any particular set of conditions the ultimate product is an equilibrium mixture the composition of which is the same, no matter whether the starting material is the ester (III) or a mixture of equivalent quantities of the esters (I) and (II).

The proof of the reversibility of this reaction is of interest because it completes the analogy with three-carbon tautomerism. For example, the equilibrium represented by equation (A) is strictly comparable with the equilibrium, the existence of which is clearly proved, if further proof be needed, by the very recent experiments of Feist and his collaborators (*Annalen*, 1922, **428**, 25, 40, 59, 68), between the labile glutaconic esters (IV) and (V) :



Both reactions are reversible, but reaction (A) is intermolecular, whilst reaction (B) is intramolecular; that is, we think, the whole of the formal difference between them. It is precisely this difference, however, which renders the second reaction alone capable of being brought within the philosophical (as distinguished from the historical) definition of tautomerism as reversible change between isomerides.

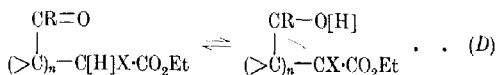
From this point of view, then, the glutaconic acid change is an intramolecular Michael condensation. Clearly, however, it is but one of a large number of theoretically possible intramolecular changes, of which reaction (A) is the intermolecular prototype; for the two carbon atoms which become joined by a single bond in the reaction represented by equation (A) read from left to right, and by a double bond in the corresponding change expressed in equation (B), might, one may suppose, become involved in a *cyclopropane* ring, or a *cyclobutane* ring, or in larger rings, as a result of intramolecular condensation. Since this internal condensation would be of the same nature as a Michael reaction, we should expect it to be reversible :



Obviously equation (B) corresponds with the particular case in which  $n = 0$ . The unsaturated open-chain compound (VI) and the saturated cyclic compound (VII) are isomerides, and equation (C) must therefore be regarded as expressing a kind of tautomerism; clearly, moreover, the relationship represented belongs to the group of phenomena to which the name ring-chain tautomerism has been applied. All the examples of ring-chain tautomerism hitherto recorded belong to the keto-enol\* type, an instance of which (the simplest yet described) has been given by Thorpe and Deshapande (this vol., p. 1430):

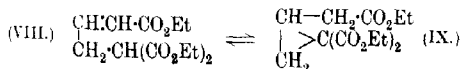


Keto-enol ring-chain tautomerism may be formulated in general terms as follows [equation (D)]:



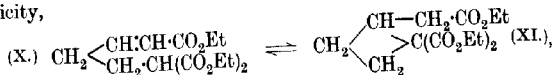
and there is ample evidence at the present time of its occurrence. Equations (C) and (D) are precisely similar, and the former is therefore to be regarded, not only as the general expression for an internal Michael condensation, but also, on still broader lines, as the fundamental formula for three-carbon ring-chain tautomerism. From what has been written with regard to the relationship of three-carbon ring-chain tautomerism to the ordinary direct and retrograde Michael reaction (A), to the tautomerism of the glutamic esters (B), and to keto-enol ring-chain tautomerism (D), there seems every reason to believe in the possibility of both the occurrence and reversibility of the reactions expressed in equation (C), and, indeed, in the reality of the general phenomenon which this equation represents.

The simplest imaginable instance illustrating the type of tautomerism under discussion would be that provided by the interconversion of the unsaturated straight-chain ester (VIII) with the saturated cyclopropane ester (IX):



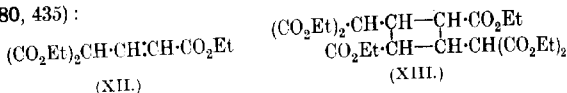
\* The term "keto-enol" was used in Part I of this series to indicate tautomeric change between an open-chain ketone and its hydroxy-ring isomeride in order to illustrate the type of phenomenon involved. The term is, however, open to the objection that the "enol" form is not in this case an unsaturated alcohol, and, for this reason, it is proposed in future to use the term "keto-cyclol" to denote the new kind of tautomerism.

We have not yet synthesised either of these substances, because on consideration it seemed that in the case next in order of simplicity,

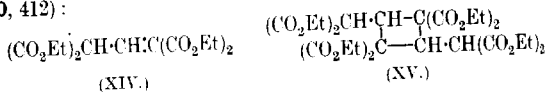


there were facts on record which placed in our hands a ready means of investigating the general principle without any recourse to preliminary synthetical experiments.

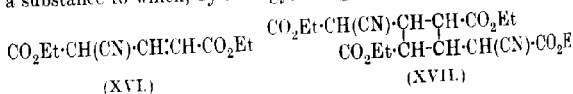
At an early period, Guthzeit found that ethyl  $\alpha$ -carboxyglutamate (XII), on keeping at the ordinary temperature for a year, or on treating with a small amount of piperidine for a much shorter period, became transformed into a liquid "bimeric" ester, to which formula (XIII) was subsequently assigned (Guthzeit, *Ber.*, 1898, 34, 2753; Guthzeit, Weiss, and Schäfer, *J. pr. Chem.*, 1909, [ii], 80, 435):



Ethyl dicarboxyglutamate (XIV) appeared to undergo a similar change, but more slowly. In this case, however, the condensation product, represented by formula (XV), was a solid, m. p.  $103^\circ$ , from which a stereoisomeride, m. p.  $87^\circ$ , could be obtained. In the absence of piperidine, the conversion was appreciable after one year, whilst if piperidine were added, the change proceeded to the extent of 75–80 per cent. in seven weeks (Guthzeit, *Ber.*, 1901, 34, 675; Guthzeit, Weiss, and Schäfer, *J. pr. Chem.*, 1909, [ii], 80, 412):



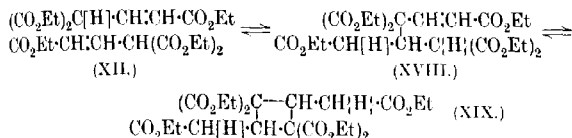
More recently, Verkade showed (*K. Akad. Wetensch. Amsterdam* 1919, 27, 1133) that  $\alpha$ -cyanoglutaconic ester (XVI) undergoes conversion with great ease, even in the absence of piperidine, into a substance to which, by analogy, was given formula (XVII):



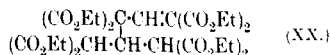
In none of these cases has any inquiry been made into the cause or mechanism of the changes observed. The term "polymerism" seems to have been considered sufficiently self-explanatory, and no attempt has been made to show why some glutaconic ester

"polymerise" and others do not, or why the rapidity and completeness of the process vary in the way they do in the different instances. Neither has any one previously endeavoured to demonstrate the ordered solidarity of the reactions under discussion with any large and well-worked-out group of phenomena.

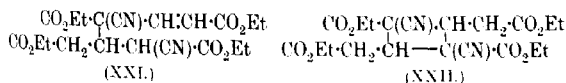
The fundamental circumstance is that a glutaconic ester contains within its molecule both the residues by the interaction of which a Michael condensation takes place. For instance,  $\alpha$ -carboxyglutaconic ester (XII) contains a malonic ester residue and an acrylic ester residue; if the reaction between these is intramolecular, three-carbon tautomerism, in the sense of equation (B), is the result; but if the malonic ester residue of one molecule reacts with the acrylic ester residue of another molecule, the product (XVIII) is a substance (a derivative of the ester X) capable of exhibiting ring-chain, three-carbon tautomerism (equation C) with its cyclic isomeride XIX (the corresponding derivative of ester XI):



The last reaction is an internal Michael condensation, and the evidence for its reversibility is given on pp. 1775, 1776 and 1785, 1786. However, it may be stated at once that the experiments described in this paper prove quite conclusively that the above view of the mechanism of the reaction is the true one. It is necessary, therefore, to revise the formula (XIII) proposed by Guthzeit, Weiss, and Schäfer for the so-called "bimeride" of  $\alpha$ -carboxyglutaconic ester. Formula (XV) stands correct, but the formation of the substance from ethyl dicarboxyglutaconate must be preceded by the production of the open-chain isomeride (XX), to which further reference will be made below (pp. 1775, 1776, and 1777):



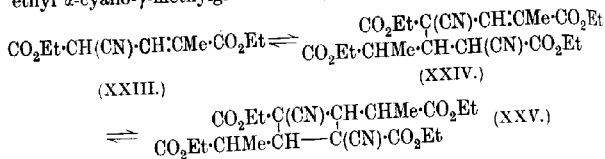
To Verkade's compound must be given the formula (XXII), the intermediate compound being the unsaturated ester (XXI),



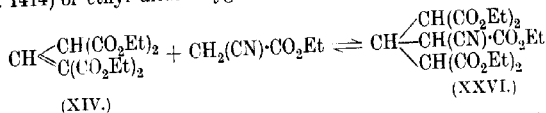
and we may include here the example described hereunder, in which



the substances (XXIV) and (XXV) are successively produced from ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate (XXIII) :

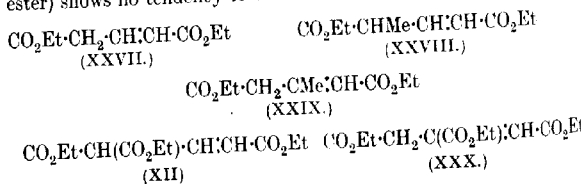


The action of piperidine in promoting these condensations is easily understood. As Knoevenagel and Mottek first showed (*Ber.*, 1904, **37**, 4464), piperidine is a powerful catalyst for the Michael condensation, and in many cases can be used with advantage in place of the sodium ethoxide more commonly employed. Its behaviour in the cases now under discussion is well illustrated by the condensation recently described (Ingold and Perren, this vol., p. 1414) of ethyl dicarboxylglutaconate with ethyl cyanoacetate :

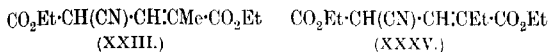
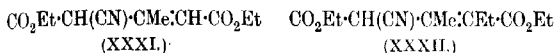


This condensation takes place with ease in the presence of piperidine, and there can be no question but that the effect of piperidine on the reaction between two molecules of dicarboxylglutaconic ester is of a precisely similar character. The reasons for the use of piperidine in place of sodium ethoxide in these cases are given on pp. 1774 and 1775.

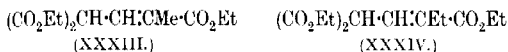
It seemed at first sight that one of the main theoretical difficulties in connexion with the study of these condensations would be the interpretation of the apparently fortuitous way in which tendency towards self-condensation is linked with structure. The facts are as follows. Glutaconic ester itself (XXVII) does not undergo self-condensation; neither does  $\alpha$ -methylglutaconic ester (XXVIII), nor the labile form of  $\beta$ -methylglutaconic ester (XXIX).  $\alpha$ -Carboxylglutaconic ester (XII) (*isoaconitic ester*), however, condenses with facility; yet  $\beta$ -carboxylglutaconic ester (XXX) (*aconitic ester*) shows no tendency to condense :



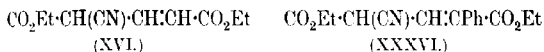
Neither  $\alpha$ -cyano- $\beta$ -methylglutaconic ester (XXXI) nor  $\alpha$ -cyano- $\beta$ -methyl- $\gamma$ -ethylglutaconic ester (XXXII) undergoes self-condensation, but  $\alpha$ -cyano- $\gamma$ -methylglutaconic ester (XXIII) condenses very easily; nevertheless,  $\alpha$ -cyano- $\gamma$ -ethylglutaconic ester (XXXV) shows no tendency to condense:



Although both  $\alpha$ -carboxyglutaconic ester (XII) and  $\alpha$ -cyano- $\gamma$ -methylglutaconic ester (XXIII) undergo self-condensation with ease,  $\alpha$ -carboxy- $\gamma$ -methylglutaconic ester (XXXIII) shows not the slightest tendency to do so; the  $\alpha$ -carboxy- $\gamma$ -ethyl derivative (XXXIV) shares this property, but the  $\alpha\gamma$ -dicarboxy-compound (XIV) condenses with moderate ease:



Ethyl  $\alpha$ -cyanoglutaconate (XVI) condenses so rapidly that it is almost impossible to isolate it; its  $\gamma$ -methyl derivative also condenses; its  $\gamma$ -ethyl derivative does not; its  $\gamma$ -phenyl derivative (XXXVI) shows a (doubtful) very slight tendency towards self-condensation:



In considering these facts, it is necessary to take into account the conditions which govern the occurrence of any Michael reaction. These have been broadly indicated in the three papers on the subject which have already appeared. The main points are as follows:

(a) The *acetic* ester which takes part in a condensation must contain a negative substituent such as a carboxy- or cyano-group to confer the necessary mobility on the adjacent hydrogen atom; the cyano-group is by far the more effective (compare, for instance, the reactivity of ethyl cyanoacetate with that of ethyl malonate).

(b) The *acrylic* ester involved should be only lightly substituted:

(i) The presence of a  $\beta$ -substituent, particularly two  $\beta$ -substituents, considerably reduces the tendency towards condensation. The effect is apparently a spatial one; the larger are the groups the stronger is the inhibition.

(ii) The presence of an  $\alpha$ -substituent greatly inhibits condensation.

ation, the magnitude of the effect depending on the size of the group as under (i).

(iii) The simple spatial relationships noted under (i) and (ii) break down in the case of strongly electronegative substituents such as the carbethoxy- and cyano-groups, which inhibit condensation perceptibly but very slightly (compare, for instance, the condensation of ethyl malonate with ethyl acrylate, crotonate, and fumarate). We must postulate here some kind of polar effect superimposed on, or in some other way modifying, the simple spatial phenomenon.

By applying these principles to the cases under discussion, we obtain in the first place a complete account of the behaviour of all the glutaconic esters which have as yet been examined with regard to their capacity for self-condensation. The rules are sufficiently definite, moreover, to enable one to predict the susceptibilities of those glutaconic esters which have not yet been examined in this connexion.

According to rule (a), it is a necessary condition for self-condensation that the portion of the glutaconic ester molecule which may be regarded as its acetic ester residue should contain a negative substituent such as the carbethoxy- or the cyano-group; that is to say, one or other of these groups must be present in what is usually termed the  $\alpha$ -position. In agreement with this inference, we find that every one of the glutaconic esters which have been shown to undergo self-condensation contains an  $\alpha$ -carbethoxy- or  $\alpha$ -cyano-group; no glutaconic ester which lacks a negative  $\alpha$ -substituent of this sort has ever been shown to undergo this type of change. According to rule (a),  $\alpha$ -cyanoglutaconic esters should undergo condensation more readily than the corresponding  $\alpha$ -carbethoxy-compounds. Actually, ethyl  $\alpha$ -cyanoglutaconate passes into its condensation product in minutes in the absence of a catalyst and instantaneously in the presence of piperidine, whilst ethyl  $\alpha$ -carbethoxyglutaconate changes in the course of months in the absence of a catalyst and in days in the presence of piperidine. Another instance of the same kind is mentioned below.

A  $\beta$ -substituted glutaconic ester is to be regarded as a  $\beta\beta$ -disubstituted acrylic ester, and should, according to rule [b(i)] above, show but little tendency to condense, even if the conditions required by rule (a) are fulfilled. As a matter of fact, all the  $\beta$ -substituted glutaconic esters which have as yet been examined have failed to exhibit any tendency towards self-condensation. (The effect of the presence in the  $\beta$ -position of the strongly electronegative groups referred to under [b(iii)] has not yet been investigated.)

A  $\gamma$ -substituted glutaconic ester may be regarded as an  $\alpha$ -substituted acrylic ester, and according to rule [b(ii)] condensation should be inhibited by the presence in this position of groups (other than those the effect of which is expressed in rule [b(iii)]) of considerable atomic volume. In agreement with this conclusion, we find that if the  $\alpha$ -substituent required by rule (a) is a carboethoxy-group, any  $\gamma$ -alkyl group, even the methyl group, is sufficient to prevent condensation; if, however, the  $\alpha$ -substituent is the more strongly reaction-promoting cyano-group, then not only the  $\gamma$ -hydrogen compound but also the  $\gamma$ -methyl compound gives condensation products, although  $\gamma$ -alkyl groups larger than methyl inhibit the reaction.

Finally, the behaviour of compounds containing a carboethoxy- or a cyano-group in the  $\beta$ - or  $\gamma$ -position should, by rule [b(iii)], be generally similar to that of the corresponding substance which has a hydrogen atom in place of this group. The similarity of behaviour of ethyl  $\alpha$ -carboxyglutaconate and ethyl  $\alpha\gamma$ -dicarboxyglutaconate forms an instance of the application of this rule, but it should be added that glutaconic esters of the type in question have not as yet been extensively examined.

These rules and the facts which they interpret may be summarised for convenience in tabular form :—

(A.) *Glutaconic esters without a negative  $\alpha$ -substituent do not condense.*

The esters  $\left\{ \begin{array}{l} \text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{CO}_2\text{Et} \end{array} \right\}$  do not condense.

(B.) *Glutaconic esters \* with a  $\beta$ -substituent do not condense.*

The esters  $\left\{ \begin{array}{l} \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMe}\cdot\text{CEt}\cdot\text{CO}_2\text{Et} \end{array} \right\}$  do not condense.

(C.) *Glutaconic esters \* [outside classes (A) and (B)] with a  $\gamma$ -substituent condense if it is sufficiently small.*

(i)  *$\alpha$ -Carboxyglutaconic esters :—*

The ester  $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  condenses.

The esters  $\left\{ \begin{array}{l} (\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Et} \\ (\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}\cdot\text{CEt}\cdot\text{CO}_2\text{Et} \end{array} \right\}$  do not condense.

(ii)  *$\alpha$ -Cyanoglutaconic esters :—*

The esters  $\left\{ \begin{array}{l} \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CH}\cdot\text{CMe}\cdot\text{CO}_2\text{Et} \end{array} \right\}$  condense.

The esters  $\left\{ \begin{array}{l} \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CH}\cdot\text{CEt}\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{Et} \end{array} \right\}$  do not condense.

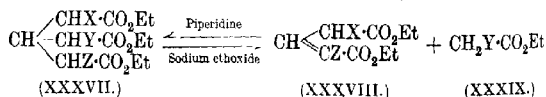
\* Excepting those included under (D).

(D) *Glutaconic esters with strongly negative \*  $\beta$ - or  $\gamma$ -substituents behave similarly to the corresponding  $\beta$ - or  $\gamma$ -hydrogen compounds.*

The ester  $(\text{CO}_2\text{Et})_2\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$  condenses.

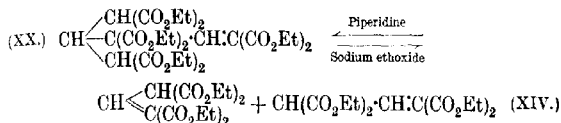
Thus it appears that all the facts relating to the self-condensation of the glutaconic esters are in complete and detailed agreement with the general principles which have been reached in other ways, and it does not seem probable that any future development will necessitate a very serious modification in the guiding rules. Evidently, examples of this kind of self-condensation will always be comparatively scarce, because so many conditions have to be satisfied; but one may venture to predict that it will be found to be observable, for example, in the following cases: ethyl  $\alpha$ -cyano- $\gamma$ -carboxyglutaconate, ethyl  $\alpha$ -cyano- $\beta$ -carboxyglutaconate, and ethyl  $\alpha\beta$ -dicyanoglutaconate.

In a previous communication (this vol., p. 1414), it was clearly proved that the equilibria attained in Michael condensations between esters were often of an entirely different order from the equilibria between corresponding sodio-derivatives. That this must be so follows from considerations relating to the heats of formation of the sodium compounds. It is the case, for instance, in the formation of the substituted methanetriacetic ester (XXVI), which cannot be obtained by condensation in the presence of sodium ethoxide owing to the adverse character of the equilibrium between the sodium compounds. The equilibrium between the esters themselves, however, is much more favourable to the formation of the condensation product, which may readily be prepared from the free esters by the aid of the catalyst piperidine. The relationship appears to be a general one. It does not seem possible to obtain any tri-substituted methanetriacetic ester of type (XXXVII) by the condensation of sodium derivatives owing to the large tendency towards fission into simpler esters, (XXXVIII) and (XXXIX), by the retrograde reaction. Nevertheless, the two esters (XXXVIII) and (XXXIX) may condense in the free state under the influence of some catalyst such as piperidine to form considerable amounts of the methanetriacetic ester (XXXVII). The general result, therefore, is that the condensation which takes place in the presence of piperidine is reversed by sodium ethoxide:

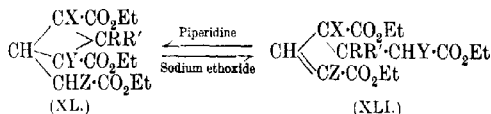


\* The term "negative" is used in connexion with groups such as CN and  $\text{CO}_2\text{Et}$ .

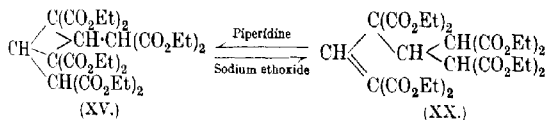
Now all the compounds (XVIII, XX, XXI, and XXIV) which constitute the first products of the self-condensation of the glutaconic esters (they constitute, also, the open-chain individual of the ultimate ring-chain system) are methanetriacetic esters similar to (XXXVII). It is therefore to be expected that these substances will be formed from glutaconic esters in the presence of piperidine, and decomposed into glutaconic esters in the presence of sodium ethoxide. Reference to the experimental part of this paper will show that this is the case. The ester (XX), which is formed in considerable amount from ethyl dicarboxylglutaconate with the aid of piperidine, and can be isolated in a moderately pure form, is converted almost completely into ethyl dicarboxylglutaconate by sodium ethoxide :



There is every reason to believe that similar phenomena appear in the cyclic series, and that, for example, methanetriacetic esters of type (XL) exhibit the following analogous relationships :



Obviously, all the *cyclobutane* esters of which this paper treats (XV, XIX, XXII, XXV, and three others) are methanetriacetic esters of type (XL), whilst their open-chain isomerides (XX, XVIII, XXI, and XXIV) belong to type (XLI), and therefore it is to be expected that the ester (XV), for example, would show the following relations with the ester (XX) :



The degradation effected by sodium ethoxide is therefore progressive (for example,  $\text{XV} \rightarrow \text{XX} \rightarrow \text{XIV}$ ), and there is no difficulty in understanding the fact that all the *cyclobutane* esters dealt with in this paper are completely disrupted by sodium ethoxide into the glutaconic esters from which they were originally prepared.

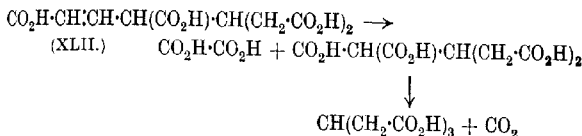
It has been shown that the succession of intermolecular and

intramolecular Michael condensations by means of which the *cyclobutane* esters are formed can be completely reversed by changing the experimental conditions. It remains now to examine the evidence for the existence of a definite equilibrium under any one particular set of conditions. Consider the pair of isomerides (XV) and (XX). The *cyclobutane* ester (XV) is a solid (m. p.  $103^{\circ}$ ), whilst the open-chain ester (XX) is a liquid, so that when crystallisation of the solid ester has once commenced the equilibrium in the liquid phase becomes continuously disturbed until the whole of the material is converted into the solid isomeride. By employing a solvent, however, or by allowing interconversion to proceed at somewhat above the ordinary temperature, it is easy to show that an equilibrium is reached containing upwards of 80 per cent. of the cyclic compound and 10–20 per cent. of its open-chain isomeride, which can be separated from the mixture in the manner described on pp. 1785, 1786. The equilibrium is substantially the same whether piperidine is present or not, and it is also the same whether the starting material is the *cyclobutane* ester or the open-chain ester or any mixture of them.

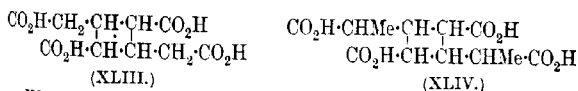
Plainly, therefore, these esters satisfy all the requirements of what we have termed the philosophical definition of a tautomeric substance, and there is no distinction to be drawn, from this point of view, between, let us say, the *cyclobutane* ester (XV) and Knorr's ketonic ethyl acetoacetate. Both esters, in the fused or dissolved state, undergo reversible isomeric change and reach equilibria dependent only on the temperature and the solvent. In both cases, the reaction, although hastened by the deliberate addition of a catalyst, takes place at a more or less considerable speed without this aid. In both cases, also, the mechanism of the change is extremely simple, involving nothing more than the transmigration of a mobile hydrogen atom. Finally, in both cases the pure liquid esters exhibit the phenomenon, so there can be no question of a composite reaction, involving, for example, the addition and subsequent removal of water. This matter is an important one, because the greatest difficulty which at present stands in the way of the general recognition of ring-chain tautomerism as a widespread phenomenon, depending, like ordinary keto-enol tautomerism, on the mobility of a hydrogen atom, is the possibility that interchange between the individuals may be a composite process. The molecular changes which lie at the basis of the mutarotation of the sugars have been explained by Meyer and Jacobsen ("Organischen Chemie," 2<sup>te</sup> Aufl., I, 2, 927) as simple ring-chain processes, but most workers in the sugar group seem to have regarded addition and elimination of water

as the mechanism of these changes (compare Lowry, T., 1903, 87, 1316). In any case, this possibility cannot be ignored, because the reactions considered take place in the presence of water, and so do all those to which attention has previously been directed in the papers of this series. Now, however, for the first time, it seems that we have a clear case of reversible interconversion between liquid substances, the one an open-chain compound and the other a cyclic compound, by the simple transmigration (for surely no other interpretation seems possible) of a mobile hydrogen atom.

It remains to be added that just as the ketonic and enolic forms of ethyl acetoacetate each exhibit their own distinctive chemical reactions corresponding with their respective structural formulæ, so the two individuals of the ring-chain system each display all the special characteristics expressed by the formulæ assigned to them. The open-chain compound (XX), for instance, is highly unsaturated, and on hydrolysis by means of mineral acids yields an acid (XLII) the constitution of which is clearly proved by the manner of its oxidation. On treatment with cold alkaline permanganate, it takes up four atoms of oxygen and is converted almost quantitatively into methanetricarboxylic acid and oxalic acid, one carboxyl group being eliminated as carbon dioxide subsequently to fission at the double bond:



On the other hand, the cyclic compound (XV) is fully saturated and resists the action of permanganate. On hydrolysis by mineral acids, it yields a saturated acid of the *cyclobutane* series. This acid, 2:4-dicarboxycyclobutane-1:3-diacetic acid (XLIII), has now been obtained in all five of the theoretically possible stereoisomeric modifications, the formation and mode of interconversion of which are expressed in the table which follows. We have employed Greek prefix-letters for convenience in distinguishing the compounds under discussion. Similarly, the *cyclobutane* ester (XXV) undergoes hydrolysis by mineral acids to an acid (XLIV) which should also occur in five modifications, although up to the

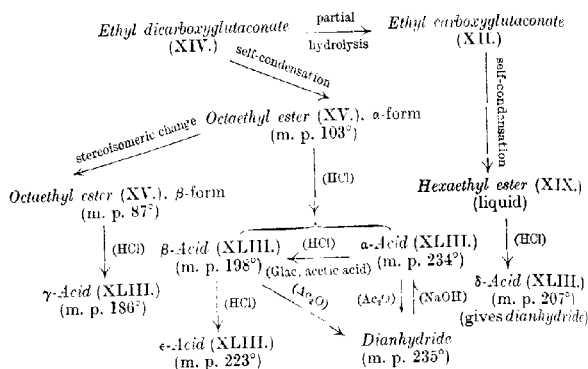


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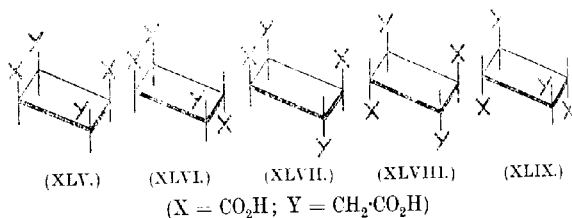


present time only two of these have been isolated. They occur together in the crude hydrolysis product, and may readily be separated by taking advantage of the large difference in the ease with which they yield anhydrides.

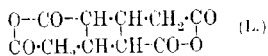
### FORMS OF THE ACID (XLIII).



These relationships strongly suggest (although, of course, they do not finally prove) the stereoisomeric configurations of the different acids. The five possible formulæ are as follow :

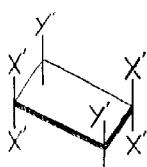


Evidently, the  $\alpha$ -acid, which is the first tetrabasic hydrolysis product of the  $\alpha$ -ester, m. p.  $103^\circ$ , is a double-*cis*-acid (XLV); it yields a dianhydride (L), and on heating with hydrochloric acid changes

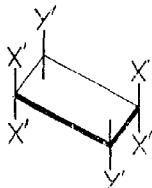


successively into the  $\beta$ -acid (XLVI) and the  $\epsilon$ -acid (XLIX) by the passage of the two carboxyl groups to the *trans*-position. There are only two possible configurations for the octaethyl ester, namely

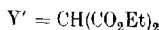
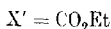
(LI) and (LII), and we may assume for the moment that the less stable  $\alpha$ -modification, m. p.  $103^\circ$ , is the *cis*-form (LI). This view



(LI.)



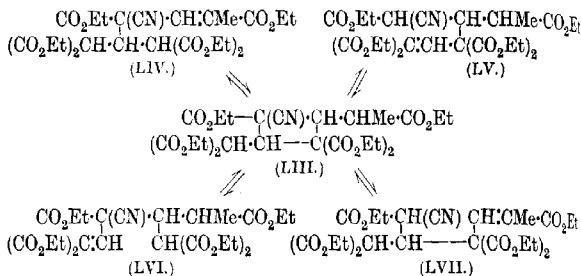
(LII.)



is rendered probable by several circumstances. For example, it is well known that carboxy groups in *trans*-positions with respect to the substituents attached to the adjacent carbon atoms of an alicyclic ring are always hydrolysed more readily, other conditions being the same, than corresponding groups in *cis*-positions, which are protected, it is supposed, by steric inhibition. The hydrolysis and subsequent elimination of the least protected carboxy groups from an ester of the configuration represented by formula (LI) would lead to the formation of a tetrabasic acid having the configuration (XLV), which we have assigned, for other reasons, to the product actually obtained. Similar considerations applied to the ester (LII), which must be the  $\beta$ -ester, m. p.  $87^\circ$ , show that this substance should yield an acid the configuration (XLVII) of which is not only different from that of any of the three acids derived from the  $\alpha$ -ester, but different in such a way that interconversion is not possible by stereomigration of a carboxy-group. This corresponds with the  $\gamma$ -acid, and we are led to assign formula (XLVII) to this acid, and formula (XLVIII) to the  $\delta$ -acid. Both these acids are stable towards hydrochloric acid, as the assigned configurations indicate, and the  $\delta$ -acid gives a dianhydride, as it should.

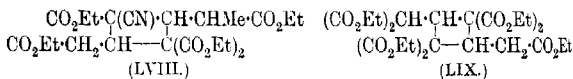
In addition to the *cyclobutane* esters mentioned above, three others are described in the experimental portion of this paper. It was anticipated that glutaconic esters which condense with themselves would, if their reactivities were of a similar order, exhibit a definite tendency to condense with each other. Ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate, ethyl  $\alpha\gamma$ -dicarboxyglutaconate, and ethyl  $\alpha$ -carboxyglutaconate all undergo self-condensation at fairly comparable rates, and therefore the experiment was tried of mixing them together in pairs. In each case, a mixed condensation product was obtained. Particular interest attaches to the condensation product of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate with ethyl

dicarboxyglutaconate. It is a liquid at the ordinary temperature and consists of an equilibrium mixture of a somewhat complex character. Theoretically, the *cyclobutane* ester (LIII) should be in equilibrium with as many as four open-chain isomerides (LIV, LV, LVI, and LVII) :



and there can be little doubt that the above scheme truly represents the condition, although, owing to the difficulty of the experimental investigation, the evidence is as yet incomplete.

The cyclic condensation products of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate with ethyl  $\alpha$ -carboxyglutaconate (LVIII), and of ethyl  $\alpha$ -dicarboxyglutaconate with ethyl  $\alpha$ -carboxyglutaconate (LIX) are crystalline (m. p.  $81^\circ$  and  $92^\circ$ , respectively), but on keeping in the fused condition they soon begin to exhibit the reactions of their unsaturated isomerides.



These examples are sufficient to show that the formation or the disruption of a homocyclic ring is not invariably the clean-cut, irreversible process that it has hitherto been imagined. Provided that the substituents are suitable, an alicyclic molecule may open and close again, under ordinary conditions of temperature and in the complete absence of any reagent, and may continue to open and close for an indefinite period in statistical equilibrium with its neighbours, unless crystallisation determines once and for all the course of the change.

#### EXPERIMENTAL.

##### (A) The Preparation of Alkyl-, Carboxy-, and Cyano-glutaconic Esters.

- (i) *Esters which do not contain a Negative  $\alpha$ -Substituent.*—  
 (a) Ethyl glutaconate was prepared from acetonedicarboxylic

acid by Blaise's method (*Bull. Soc. chim.*, 1903, [iii], 29, 1012), which is by far the most convenient for the purpose. (b) Ethyl aconitate was prepared by Anschütz and Klingemann's process from ethyl acetylcitrate (*Ber.*, 1885, 18, 1983). (c) Ethyl  $\alpha$ -methylglutaconate was obtained by directly esterifying the corresponding acid (Thole and Thorpe, T., 1911, 99, 2197). (d) Ethyl  $\beta$ -methylglutaconate (the labile form) was prepared by treating ethyl isodehydracetate with sodium ethoxide as described by Bland and Thorpe (T., 1912, 101, 1565).

(ii) *Esters containing a  $\beta$ -Alkyl Group.*—(e) Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate was prepared by condensing ethyl cyanoacetate with ethyl acetoacetate (Rogerson and Thorpe, T., 1905, 87, 1687).

(f) Ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\gamma$ -ethylglutaconate was prepared from ethyl cyanoacetate and ethyl ethylacetoacetate (T., 1905, 87, 1712).

(iii)  *$\alpha$ -Carboxyglutaconic Esters (without a  $\beta$ -Alkyl Group).*—

(g) Ethyl  $\alpha$ -carboxyglutaconate (ethyl isoaconitate) was prepared by the method of Guthzeit and Dessel (*Ber.*, 1889, 22, 1413; see also Ingold and Perren, T., 1921, 119, 1591). (h) Ethyl  $\alpha$ - $\gamma$ -dicarboxyglutaconate was obtained by the improved modification (Ingold

and Perren, *loc. cit.*) of the original process described by Conrad and Guthzeit (*Ber.*, 1882, 15, 281). (i) Ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate was obtained by treating the methyl derivative of the preceding one with sodium ethoxide (Thole and Thorpe, T., 1911, 99, 2197). (j) Ethyl  $\alpha$ -carboxy- $\gamma$ -ethylglutaconate was prepared similarly to the methyl compound (*loc. cit.*).

(iv)  *$\alpha$ -Cyanoglutaconic Esters (without a  $\beta$ -Alkyl Group).*—(k) Ethyl  $\alpha$ -cyanoglutaconate has been described previously (Ingold and Perren, *loc. cit.*). (l) Ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate was prepared by the reaction described in the previous paper (*loc. cit.*), and also by the more convenient method given below. (m) Ethyl  $\alpha$ -cyano- $\gamma$ -ethylglutaconate was prepared by condensing ethyl  $\alpha$ -carboxy- $\gamma$ -ethylglutaconate (1 mol.) with ethyl sodiocyanoacetate (2 mols.) under exactly the same conditions as were employed in the case of the lower homologue (*loc. cit.*). The quicker method described below was also used. (n) Ethyl  $\alpha$ -cyano- $\gamma$ -phenylglutaconate (see p. 1782).

(B) *The Condensation of Ethyl Sodiocyanoacetate with Esters of  $\alpha$ -Formyl-fatty Acids.*

This condensation, three examples of which are given below, leads, in general, to the production of  $\alpha$ -cyano- $\gamma$ -alkylglutaconic esters and constitutes the quickest and most inexpensive method of making these compounds. It is a simple extension of Verkade's reaction (*K. Akad. Wetensch. Amsterdam*, 1915, 18, 981).

*Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate* (XXIII).—Ethyl  $\alpha$ -formylpropionate (66 grams), which was prepared by condensing ethyl formate with ethyl propionate in the usual manner, was gradually mixed with a suspension of ethyl sodiocyanoacetate obtained by adding ethyl cyanoacetate (57 grams) to a well-cooled solution of sodium ethoxide prepared by dissolving sodium (11.5 grams) in absolute ethyl alcohol. The mixture, which contained a bright yellow, crystalline precipitate, was heated for one hour, cooled, and poured into three volumes of dilute hydrochloric acid. The oil was extracted with ether, and the extract washed with water and aqueous sodium carbonate, dried, and evaporated. The residue, on distillation, gave 23 grams of unchanged ethyl  $\alpha$ -formylpropionate and 42 grams of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate, b. p. 150–155°/11 mm. (Found: C = 58.4; H = 6.6. Calc., C = 58.6; H = 6.7 per cent.).

*Ethyl  $\alpha$ -Cyano- $\gamma$ -ethylglutaconate* (XXXV).—This ester was prepared by heating ethyl  $\alpha$ -formylbutyrate (48 grams) with a suspension of ethyl sodiocyanoacetate obtained from ethyl cyanoacetate (38 grams), sodium (7.6 grams), and ethyl alcohol (130 grams). The product, when worked up as described above, gave 35 grams of unchanged ethyl  $\alpha$ -formylbutyrate (b. p. 100°/15 mm.) and 8 grams of ethyl  $\alpha$ -cyano- $\gamma$ -ethylglutaconate, which was obtained as a colourless, mobile oil, b. p. 163°/14 mm. (Found: C = 60.4; H = 7.2.  $C_{11}H_{17}O_4N$  requires C = 60.2; H = 7.1 per cent.).

In order to confirm the constitution assigned to this ester, it was hydrolysed with 50 per cent. sulphuric acid. The product, which was extracted with ether and crystallised from water, was identified as  $\alpha$ -ethylglutaconic acid by direct comparison and by the m. p. of a mixture with a genuine specimen.

The ethyl  $\alpha$ -formylbutyrate required for the above experiment was prepared by adding a mixture of ethyl butyrate (232 grams) and ethyl formate (148 grams) during a period of five hours to a suspension of molecular sodium (50 grams) in dry ether (400 c.c.). Twenty-four hours later, the sodium salts were dissolved in water, which was separated from the ether, washed once with fresh ether, and then acidified with hydrochloric acid. The formyl ester, precipitated in this way, boiled at 100°/15 mm., the yield being 48 grams.

*Ethyl  $\alpha$ -Cyano- $\gamma$ -phenylglutaconate* (XXXVI).—Ethyl formylphenylacetate (15 grams) was heated with a suspension of ethyl sodiocyanoacetate prepared from ethyl cyanoacetate (9 grams), sodium (1.9 grams), and ethyl alcohol (25 grams). After forty-five minutes, the semi-solid mass was cooled and treated with an excess of dilute hydrochloric acid. The oil was extracted with

ether, washed with water and aqueous sodium hydrogen carbonate, and purified by distillation, when 4 grams, b. p. 200—205°/14 mm., were collected (Found: C = 68.8; H = 6.3.  $C_{16}H_{17}O_4N$  requires C = 66.9; H = 5.9 per cent.).

(c) *The Self-condensation of Glutaconic Esters, Alone and in the Presence of a Catalyst (Piperidine).*

*General Method (Catalytic).*—The ester to be investigated (20 grams) was mixed with piperidine (1.0 gram) and then allowed to remain at the ordinary temperature for one year unless it became apparent at an earlier period that self-condensation had taken place. In those cases in which the reaction product did not crystallise, self-condensation was always accompanied by a very large increase of viscosity. If at the end of a year no crystals had been deposited, the ester, whether mobile or viscous, was dissolved in ether, washed with a little dilute sulphuric acid to remove piperidine, and then recovered by drying and evaporating the ether. The residue was divided into two portions, one of which was distilled, and the other hydrolysed by means of mineral acids. If the boiling point was that of the glutaconic ester originally used, and if, also, the sole product of acid hydrolysis was a glutaconic acid, it was assumed that no self-condensation had occurred. In all cases in which self-condensation did occur acids of the *cyclobutane* series were readily isolated from the products of hydrolysis. In these instances, the following experiments were tried.

*Non-catalytic Self-condensation.*—The above experiment was repeated without, however, adding piperidine to the ester.

*Reversal of Condensation.*—This was effected by treating the *cyclobutane* ester (1 mol.) with sodium ethoxide (2 mols.). After heating for one hour, the product was poured into water and the oil extracted with ether. By distillation under diminished pressure, or by hydrolysis with mineral acid, the residue which remained when the ether extract was dried and evaporated was easily proved to consist of the expected glutaconic ester.

*Glutaconic Esters Incapable of Self-condensation.*—The following esters appeared not to have given any condensation product when the above tests were applied:

(i) *Esters which do not contain a negative  $\alpha$ -substituent*, namely, ethyl glutaconate, ethyl aconitate, ethyl  $\alpha$ -methylglutaconate, and ethyl  $\beta$ -methylglutaconate.

(ii) *Esters containing a  $\beta$ -alkyl group*, namely, ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate and ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\gamma$ -ethylglutaconate.

(iii)  *$\alpha$ -Carboxy- $\beta$ -hydroxyglutaconic esters*, namely, ethyl  $\alpha$ -carboxy- $\gamma$ -methylglutaconate and ethyl  $\alpha$ -carboxy- $\gamma$ -ethylglutaconate.

(iv)  $\alpha$ -Cyano- $\beta$ -hydroxyglutaconic esters, namely, ethyl  $\alpha$ -cyano- $\gamma$ -ethyl glutaconate and ethyl  $\alpha$ -cyano- $\gamma$ -phenylglutaconate. (Actually, this ester gave a very small quantity of a crystalline compound, m. p.  $123^\circ$ , which may have been a self-condensation product, but the amount was insufficient for proper investigation.)

*Glutaconic Esters which Undergo Self-condensation.*—Definite self-condensation products were obtained in four cases, namely, ethyl  $\alpha$ -carboxyglutaconate (ethyl isoaconitate), ethyl  $\alpha\gamma$ -dicarboxyglutaconate, ethyl  $\alpha$ -cyanoglutaconate, and ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate.

(i) *Ethyl  $\alpha$ -Carboxyglutaconate* (ethyl isoaconitate).—The action of piperidine on this compound was examined by Guthzeit, Weiss, and Schäfer (*loc. cit.*). We have found that, under the standard conditions indicated above, self-condensation is practically complete after one week, whilst in the absence of a catalyst at least one year is required.

*Ethyl 2:2:4:4-tetracarboxycyclobutane-1:3-diacetate* (XIX), previously described as ethyl 2:4-dicarboxycyclobutane-1:3-dimalonate, is a colourless, fairly viscous oil which cannot be distilled without decomposition. Its molecular weight in solvents proves the absence of any appreciable quantity of ethyl carboxyglutaconate, and its cyclic structure is indicated by its hydrolysis to  $\delta$ -2:4-dicarboxycyclobutane-1:3-diacetic acid (p. 1778). Nevertheless, the ester appears to contain a certain quantity of its unsaturated isomeride, as the following tests show. With ferric chloride, the ester gives a brown coloration; this property appears to be characteristic of the unsaturated isomerides (below), and is not shown by any freshly dissolved, pure cyclobutane ester of this series. The ester decolorises a limited quantity of neutral potassium permanganate instantly; any further amount is decolorised only very slowly.

On warming with an alcoholic solution of sodium ethoxide, the ester is quickly and completely converted into ethyl carboxyglutaconate.

(ii) *Ethyl  $\alpha\gamma$ -Dicarboxyglutaconate.*—Guthzeit, Weiss, and Schäfer found (*loc. cit.*) that the action of piperidine on this substance leads to a solid ester (XV), m. p.  $103^\circ$ , which on treatment with a further quantity of piperidine in benzene solution passes into a stereoisomeric modification, m. p.  $87^\circ$ . The former gave the  $\alpha$ - and  $\beta$ -modifications, and the latter the  $\gamma$ -modification, of 2:4-dicarboxycyclobutane-1:3-diacetic acid. We have found that, under the standard conditions described on p. 1783, the formation of the ester, m. p.  $103^\circ$ , is practically complete in the course of two months, whilst in the absence of a catalyst it is just perceptible

after one year. In the case of this condensation reversibility is easily demonstrated, and its retarding influence can be appreciated by freezing out and removing the solid ester at regular intervals, a procedure which greatly hastens the reaction. If the temperature is such that crystallisation does not occur at any stage, the formation of the ester, m. p.  $103^{\circ}$ , remains incomplete and a definite proportion of ethyl dicarboxyglutaconate may be recovered as its sodio-derivative by washing with sodium carbonate (see below). In all condensations in which piperidine is employed, a small quantity of the material undergoes a side reaction leading to ethyl piperidinomethylenemalonate,  $C_5H_{10}>N\cdot CH:C(CO_2Et)_2$ , which crystallises from benzene in pale yellow, rhombohedral plates melting with decomposition at  $216^{\circ}$  (Found: C = 61.2; H = 8.3.  $C_{13}H_{21}O_4N$  requires C = 61.2; H = 8.2 per cent.).

$\alpha$ -Ethyl 2:2:4:4-tetracarboxycyclobutane-1:3-dimalonate (XV), m. p.  $103^{\circ}$ , is quite stable towards neutral permanganate and gives no colour with ferric chloride in freshly prepared solution. The product of hydrolysis by acids consists solely of the two saturated cyclobutane acids mentioned above. When kept in the fused condition, however, or in solution (preferably in the presence of a small amount of piperidine), it develops the capacity for reducing permanganate and giving a colour with ferric chloride. On cooling or evaporating the solvent, the ester does not completely solidify, and, in this condition, gives unsaturated products on acid hydrolysis. By fusing, or maintaining in solution with piperidine for a sufficiently long period, the ester, m. p.  $103^{\circ}$ , can be converted into an equilibrium mixture of the same composition, so far as we have been able to find, as that obtained by the self-condensation of ethyl dicarboxyglutaconate under the same conditions. This mixture contains roughly 80 per cent. of the cyclobutane ester, which can be isolated in the crystalline condition, upwards of 10 per cent. of the unsaturated isomeride described below, and a small amount of ethyl dicarboxyglutaconate.

On warming with an alcoholic solution containing sodium ethoxide (2 mols.), the cyclobutane ester is completely converted into ethyl sodiodicarboxyglutaconate.

*Ethyl  $\alpha\gamma\gamma\epsilon$ -Hexacarboxy- $\Delta^5$ -pentene- $\delta$ -malonate (XX).*—The equilibrium mixture obtained either from the cyclobutane ester or from ethyl dicarboxyglutaconate was first washed with dilute sulphuric acid to remove the piperidine, and then cooled in a freezing mixture in order to remove the main bulk of the cyclobutane ester by crystallisation. The liquid esters were dissolved in ether and shaken with sodium carbonate, which causes ethyl sodiocarboxyglutaconate to be precipitated, then recovered by evaporating the



ether, and again cooled strongly. The ester which remained liquid after this treatment consisted essentially of ethyl hexacarboxypentenemalonate, and, although, presumably, it contained traces of the cyclic isomeride, the amount of this substance present must have been very small, for no trace of any *cyclobutane* acid could be obtained from the product of hydrolysis by acids (below).

Ethyl hexacarboxypentenemalonate is a colourless oil which gives a light brown coloration with ferric chloride and instantly reduces neutral permanganate. On leaving it in contact with a little piperidine, conversion into the cyclic isomeride takes place, the ultimate product being either a liquid equilibrium mixture, containing not only the cyclic ester but also a little ethyl dicarboxyglutaconate, or the pure crystalline *cyclobutane* ester, according to the conditions. Alcoholic sodium ethoxide rapidly converts the pentene ester into ethyl dicarboxyglutaconate.

*α,γ,ε-Tricarboxy-Δ<sup>2</sup>-pentene-8-acetic Acid* (XLII).—In order to prove the constitution of the above ester, it was hydrolysed by boiling with 20 per cent. hydrochloric acid until carbon dioxide and alcohol ceased to be evolved. The product was a syrupy acid of approximately the correct composition, but it could not be crystallised. It was therefore characterised by oxidation.

The acid was dissolved in sodium carbonate and treated with cold 1 per cent. potassium permanganate until the colour became permanent. The quantity of permanganate used corresponded with a little more than four atoms of available oxygen. The small excess of permanganate was destroyed by means of sulphur dioxide, and the oxides of manganese were collected and extracted twice by treatment with steam. The combined filtrates were acidified with hydrochloric acid, evaporated to a small bulk, neutralised with ammonium hydroxide, and treated with calcium chloride. The calcium oxalate thus precipitated was collected and identified by the usual tests. The filtrate was re-acidified and extracted with ether. The residue from the ether consisted of almost pure methanetricacetic acid (this vol., p. 1420).

(iii) *Ethyl α-Cyanoglutaconate*.—This ester undergoes self-condensation much more readily than either of the carbethoxy-compounds. When freshly regenerated from an alcoholic solution of its sodium derivative, it is a mobile oil of the correct molecular weight. Self-condensation sets in rapidly, however, and is complete before the next day.

*Ethyl 2:4-dicyano-2:4-dicarboxycyclobutane-1:3-diacetate* (XXII), which has already been described by Verkade as ethyl 2:4-dicarboxycyclobutane-1:3-dicyanodiacetate (*K. Akad. Wetensch.*

*Amsterdam*, 1919, 27, 1133), appears to be an equilibrium mixture of the cyclic ester (XXII) and its unsaturated isomeride. It gives the reactions with ferric chloride and permanganate characteristic of the unsaturated compounds of this series. However, we have not yet succeeded in finding a means of separating the two constituents.

(iv) *Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate*.—When this substance is kept at the ordinary temperature without the addition of a catalyst, crystals of the self-condensation product begin to be deposited after one month; at the end of three months the whole mass is solid. When condensed in the presence of piperidine under the standard conditions described above, crystals appear in two to three hours, whilst in twenty-four to thirty-six hours the change is complete.

*Ethyl 2:4-dicyano-2:4-dicarboxycyclobutane-1:3-di- $\alpha$ -propionate* (XXV), obtained as described above, crystallises in two forms, long, silky needles, and small, glistening plates. Both forms, as well as a mixture of the two, melt at  $87^{\circ}$  (Found: C = 58.4; H = 6.5;  $M$  in freezing benzene = 457.  $C_{22}H_{30}O_8N_2$  requires C = 58.6; H = 6.7 per cent.;  $M$  = 450).

When the ester is warmed for a short time with an alcoholic solution containing two molecules of sodium ethoxide, the retrograde reaction takes place and the theoretical yield of ethyl  $\alpha$ -cyano- $\gamma$ -methylglutaconate can be recovered after pouring into hydrochloric acid.

The ester gives  $\alpha$ -methylglutaconic acid when hydrolysed with alcoholic potassium hydroxide. When acids are used, the product is a mixture of the two cyclobutane acids described below.

*trans-2:4-Dicarboxycyclobutane-1:3-di- $\alpha$ -propionic Acid* (XLIV).—The cyclobutane ester (10 grams) was boiled with 100 c.c. of 20 per cent. hydrochloric acid for twenty-four hours. The product was concentrated and extracted with ether, and the extract dried with calcium chloride and evaporated. The mixture of stereoisomeric acids could not be caused to crystallise, and was therefore boiled for two hours with acetyl chloride. The *cis*-acid was thus converted into its anhydride, which dissolved in the acetyl chloride, whilst the insoluble *trans*-acid became crystalline and could be collected by filtration. After crystallisation from glacial acetic acid, it melted at  $251^{\circ}$  (Found: C = 49.9; H = 5.6;  $M$ , by titration, = 289.  $C_{12}H_{16}O_8$  requires C = 50.0; H = 5.5 per cent.;  $M$  = 288). The acid is stable towards cold alkaline permanganate.

*cis-2:4-Dicarboxycyclobutane-1:3-di- $\alpha$ -propionic Acid* (XLIV).—The filtered acetyl chloride solution was evaporated in a vacuum

over potassium hydroxide until all the acetic acid and acetyl chloride had been removed, and the residue exposed to moist air until crystalline. The acid obtained in this way melted at 144–145° after crystallisation from ether (Found: C = 49.9; H = 5.3.  $C_{12}H_{16}O_8$  requires C = 50.0; H = 5.5 per cent.). This melting point is very close to that of  $\alpha$ -methylglutaric acid (which would give similar figures on analysis), but a mixture of the two melted at 130°; moreover, the *cis*-cyclobutane acid is stable towards cold alkaline permanganate.

- (D) *Condensations between Different Glutaconic Esters: Condensation of Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate with Ethyl  $\alpha$ -Dicarboxyglutaconate, Ethyl  $\alpha$ -Dicarboxyglutaconate with Ethyl  $\alpha$ -Carboxyglutaconate, and Ethyl  $\alpha$ -Carboxyglutaconate with Ethyl  $\alpha$ -Cyano- $\gamma$ -methylglutaconate.*

*General Method.*—These condensations were carried out in the presence of piperidine by the general method described on p. 1783, with the difference that, in place of 20 grams of a pure ester, 20 grams of a mixture of two esters in equivalent proportions was used.

*Ethyl 2-Cyano-2:4:4-tricarboxycyclobutane-1-malonate-3- $\alpha$ -propionate (LIII).*—This substance, which is formed under the conditions mentioned above in the course of about two months, is a moderately viscous liquid boiling with slight decomposition at 260°/15 mm. (Found: C = 55.9; H = 6.4.  $C_{26}H_{37}O_{12}N$  requires C = 56.0; H = 6.7 per cent.). It gives a strong brownish-yellow coloration with ferric chloride and reduces permanganate and therefore may be assumed to contain at least one unsaturated isomeride in appreciable quantity. More than one appear to be present, but the investigation is still in progress.

*Ethyl 2:2:4:4-Tetracarboxycyclobutane-1-malonate-3-acetate (LIX).*—This substance was formed along with ethyl tetracarboxycyclobutanedimalonate ( $\alpha$ -form) when ethyl dicarboxyglutaconate and ethyl carboxyglutaconate were condensed together. The two esters were separated by fractional crystallisation from ether. Ethyl tetracarboxycyclobutanemalonateacetate forms long needles, m. p. 92° (Found: C = 55.3; H = 7.3.  $C_{27}H_{40}O_{14}$  requires C = 55.1; H = 6.9 per cent.), and is generally similar in its properties to ethyl tetracarboxycyclobutanedimalonate.

*Ethyl 2-Cyano-2:4:4-tricarboxycyclobutane-1-acetate-3- $\alpha$ -propionate (LVIII).*—Crystals of this ester began to appear half an hour after the commencement of the condensation, and the process was complete in less than one day. The ester was purified by crystallisation from light petroleum, from which it separated in stout

prisms, m. p.  $81^{\circ}$  (Found: C = 57.1; H = 6.7.  $C_{23}H_{33}O_{10}N$  requires C = 57.1; H = 6.8 per cent.).

(E) *Interconversion of the  $\alpha$ -,  $\beta$ -, and  $\epsilon$ -Forms of 2:4-Dicarboxycyclobutane-1:3-diacetic Acid. Properties of the  $\gamma$ -Acid and  $\delta$ -Acid.*

The  $\alpha$ - and  $\beta$ -acids are formed side by side when ethyl tetracarboxycyclobutanedimalonate ( $\alpha$ -form) is hydrolysed with boiling hydrochloric acid. Prolonging the boiling increases the proportion of the  $\beta$ -acid, since the  $\alpha$ -acid readily undergoes conversion into its isomeride on boiling with 20 per cent. hydrochloric acid. The same change takes place on boiling a concentrated acetic acid solution of the  $\alpha$ -acid.

*Dianhydride of 2:4-Dicarboxycyclobutane-1:3-diacetic Acid (L).*—The same dianhydride is produced when either the  $\alpha$ - or  $\beta$ -form of the tetrabasic acid is boiled for one hour with acetic anhydride. It crystallises on cooling and may be purified by recrystallisation from the same solvent, and then melts at  $235^{\circ}$  (Found: C = 53.5; H = 3.5.  $C_{10}H_6O_6$  requires C = 53.6; H = 3.5 per cent.).

On dissolving in warm sodium hydroxide, acidifying with hydrochloric acid, and extracting with ether, the  $\alpha$ -acid is recovered in a pure condition.

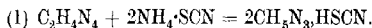
*$\epsilon$ -2:4-Dicarboxycyclobutane-1:3-diacetic Acid (XLIII).*—The  $\beta$ -acid is completely stable towards boiling 20 per cent. hydrochloric acid, but on heating at  $200^{\circ}$  with 30 per cent. acid for five hours undergoes conversion into the  $\epsilon$ -acid, which, after crystallisation from water, melts with decomposition at  $223^{\circ}$  (Found: C = 45.9; H = 4.7.  $C_{10}H_{12}O_8$  requires C = 46.1; H = 4.6 per cent.).

*The  $\gamma$ - and  $\delta$ -Acids.*—The  $\gamma$ -acid melts at  $186^{\circ}$ , a little higher than the temperature recorded by Guthzeit, Weiss, and Schäfer (*loc. cit.*). Both the  $\gamma$ -acid and the  $\delta$ -acid are stable towards hydrochloric acid at  $180^{\circ}$ . On boiling with acetic anhydride for a short time, the  $\delta$ -acid yields a crystalline dianhydride, but we are unable to quote a good analysis for this substance because its hygroscopic character rendered weighing impossible. The dianilic acid prepared from the dianhydride was amorphous. The  $\gamma$ -acid appeared to yield a hygroscopic syrupy anhydride which could not be purified.

CCXIV.—*The Preparation of Methylguanidine, and of  $\beta\beta$ -Dimethylguanidine by the Interaction of Dicyanodiamide, and Methylammonium and Dimethylammonium Chlorides Respectively.*

By EMIL ALPHONSE WERNER and JAMES BELL.

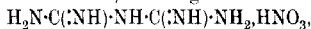
In a previous communication (T., 1920, **117**, 1133) it was shown that guanidine thiocyanate can be readily obtained, in a 90 per cent. yield, by heating a mixture of dicyanodiamide and ammonium thiocyanate at 120°, according to the equation



The reaction has now been extended to the preparation of methylguanidine,  $\text{HN}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CH}_3$ , and dimethylguanidine,  $\text{HN}\cdot\text{C}(\text{NH}_2)\cdot\text{N}(\text{CH}_3)_2$ .

In the meantime, Ewan and Young (*J. Soc. Chem. Ind.*, 1921, **40**, 1091), in addition to confirming the authors' results as regards the yield of guanidine thiocyanate, have obtained excellent yields of nitrate and sulphate of guanidine, respectively, using the corresponding salts of ammonia in place of ammonium thiocyanate in the above equation (1). With ammonium chloride, however, the yield of the guanidine salt was not so good, on account of the high temperature required to effect fusion of the mixture. In the case of methylammonium and dimethylammonium chlorides, this disadvantage does not arise, and practically quantitative yields of the substituted guanidine hydrochlorides have been readily obtained.

It was suggested by the authors (*loc. cit.*), in explanation of the mechanism of reaction (1), that depolymerisation of dicyanodiamide is the first phase in the change, the guanidine salt being formed from the union of cyanamide and the ammonium salt, thus,  $\text{CN}\cdot\text{NH}_2 + \text{NH}_3\cdot\text{HSCN} \rightarrow \text{HN}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}_2\cdot\text{HSCN}$ . Davis (*Amer. Chem. J.*, 1921, **43**, 2234) found that when a mixture of dicyanodiamide with two molecular proportions of ammonium nitrate was heated at 120° for six hours, some diguanide nitrate,

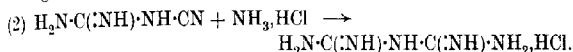


was formed, whilst a considerable proportion of the original material was unchanged. At 130°, much guanidine nitrate was formed, and at 160°, after two hours, the latter salt was produced in amount equal to 86 per cent. of the theoretical.

It was also proved that diguanide nitrate and ammonium nitrate, when fused together in molecular proportions, gave guanidine nitrate.

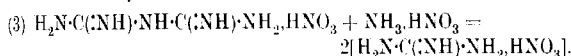
From these results, Davis concludes that "the reaction therefore is not dependent upon the depolymerisation of dicyanodiamide as Werner and Bell have supposed."

This conclusion has, we think, no foundation in fact. There is no evidence that the formation of guanidine thiocyanate is dependent on the previous formation of diguanide in the experiments described by us. If the temperature is maintained below the point ( $120^\circ$ ) at which the guanidine salt is readily formed according to equation (1), the original substances can be largely recovered unchanged. Moreover, the formation of diguanide under the conditions recorded by Davis, and the production of which was noticed also by Ewan and Young, does not prove that dicyanodiamide is not depolymerised during the progress of the reaction. Bamberger and Dieckmann (*Ber.*, 1892, **25**, 545) obtained diguanide by heating a mixture of dicyanodiamide and ammonium chloride at  $195^\circ$ . Viewing the former as cyanoguanidine,\* the change was represented thus :



According to these investigators, when guanidine hydrochloride is heated at  $180$ — $185^\circ$ , it is partly decomposed, yielding diguanide hydrochloride and ammonium chloride. This observation would seem to favour the view that guanidine is a precursor of diguanide in the reactions under consideration.

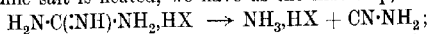
Accepting equation (2) to explain the first step in the change and assuming that diguanide there reacts with ammonia to form guanidine, Davis represents the mechanism of the final reaction, thus :



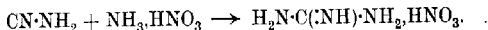
How guanidine is actually formed is not made perfectly clear by this equation.

\* The suggestion, so generally accepted, that dicyanodiamide is cyanoguanidine was originally put forward by Bamberger. The authors have very strong reasons for not accepting this view of its constitution. It is curious that no attempt has hitherto been made to prove this formula by a direct synthesis. By the action of cyanogen bromide on free guanidine, one of us (W.) has obtained evidence of the formation of the true cyanoguanidine. It is a basic substance bearing no resemblance to dicyanodiamide. It is sufficient to state here that in this reaction not a trace of dicyanodiamide was formed. Considering the stability of the latter in the static condition, it should be formed in such a reaction if it were cyanoguanidine. The theory of the mechanism of the polymerisation of cyanamide (Werner, *T.*, 1915, **107**, 716) does not suggest such a formula.

As a matter of fact, the production of diguanide from a salt of guanidine, and of guanidine from a diguanide salt by the action of heat, is a reversible change dependent on the temperature. The mechanism of the reactions is strictly comparable with that of the formation of biuret from carbamide, and of carbamide from biuret as described by Werner (T., 1913, **103**, 2275). Thus when a guanidine salt is heated, we have as the first step,



diguanide being formed by the union of cyanamide with a portion of the unchanged guanidine salt. On the other hand, a diguanide salt, when heated, is decomposed into guanidine and cyanamide; if a salt of ammonia is present as shown in equation (3), then a second molecule of guanidine results from the interaction



Whilst the formation of more or less diguanide, as an intermediate product, during the fusion of dicyanodiamide with certain salts of ammonia depends on the temperature required to initiate the change, and on the rate of its progress, at no time is there much formed under the conditions which give rise to good yields of guanidine.

The authors therefore see no reason for altering their views as regards the suggestion put forward to explain the mechanism of the formation of guanidine in their previous investigation. In the preparation of the two methylated guanidines, the formation of methyl derivatives of diguanide has been recognised during the progress of the changes.

#### EXPERIMENTAL.

*Dimethylguanidine*,  $\text{H}_2\text{N}\cdot\text{C}(\text{NH})\cdot\text{N}(\text{CH}_3)_2$ .—Expt. 1. An intimate mixture of dicyanodiamide (4.2 grams) and dimethylammonium chloride (8.15 grams) was heated in a wide-mouthed test-tube partly immersed in a bath of glycerol. The tube was closed with a cork which carried a loose-fitting thermometer, which also served as a stirrer. The mixture, which commenced to melt at about  $45^\circ$ , and was completely fused at  $130^\circ$ , was heated at  $180^\circ$  for three hours. The clear viscous product, while still warm, was dissolved in 50 c.c. of pure alcohol. The cold solution, separated by filtration from a small quantity (0.14 gram) of insoluble material,\* gave, after concentration by evaporation, a viscous residue which set to a homogeneous, crystalline mass when allowed to cool in a vacuum over sulphuric acid. The absence of unchanged dimethylammonium chloride in the product was shown by the fact that it yielded nothing

\* This consisted of impurities present in the dicyanodiamide used.

to extraction with pure dry chloroform, a solvent in which this salt is very freely soluble (Found: Cl = 28.66.  $C_3H_9N_3, HCl$  requires Cl = 28.74 per cent.).

A platinichloride was prepared in orange-red, octahedral crystals, which melted and decomposed at  $210^\circ$  [Found: Pt = 33.59.  $(C_3H_9N_3)_2, H_2PtCl_6$  requires Pt = 33.42 per cent.]. Schenck (*Arch. Pharm.*, 1912, **250**, 306) gives  $225^\circ$  for the temperature of decomposition of the platinum derivative obtained from dimethylguanidine prepared from *s*-methylthiocarbamide in accordance with the change

$$HN:C(NH_2) \cdot S \cdot CH_3 + HN(CH_3)_2 = HN:C(NH_2) \cdot N(CH_3)_2 + CH_3 \cdot SH.$$

The platinichloride prepared by us for comparison from this source was identical in appearance with that given above, and melted at the same temperature ( $210^\circ$ ). The accuracy of the thermometer used by us was tested by means of pure substances of known melting points between  $200^\circ$  and  $230^\circ$ .

A picrate prepared from the fusion product melted at  $227^\circ$ . Schenck gives  $230^\circ$  for the picrate of dimethylguanidine prepared by this method.

*Formation of Dimethyldiguanide.*—Expt. 2. Under the conditions described above, the yield of dimethylguanidine hydrochloride is practically quantitative. When the fused mixture of dicyanodiamide and dimethylammonium chloride was maintained for three and a half hours at  $120^\circ$ , a considerable residue (5.5 grams) was left after extraction of the product with alcohol as in expt. 1. By crystallisation from water, dimethyldiguanide hydrochloride was obtained in colourless, glistening prisms which melted at  $232^\circ$  (Found: Cl = 21.60.  $C_4H_{11}N_5, HCl$  requires Cl = 21.45 per cent.). The picrate, pale yellow needles from water, melted at  $219^\circ$ .

*Preparation of Methylguanidine*,  $H_2N \cdot C(NH) \cdot NH \cdot CH_3$ .—Expt. 3. A mixture of dicyanodiamide (4.2 grams) and methylammonium chloride (6.75 grams) was dealt with as in expt. 1. The mixture, which commenced to melt at  $85^\circ$ , and was completely fused at  $125^\circ$ , was heated for three hours at  $180^\circ$  to complete the interaction. The alcoholic solution of the product, filtered to remove a trace of impurity, gave, after evaporation of the solvent, a crystalline residue of pure methylguanidine hydrochloride. The dry salt is very hygroscopic (Found: Cl = 32.48.  $C_2H_7N_3, HCl$  requires Cl = 32.41 per cent.). A platinichloride was prepared, deep orange-red, stout, rhombic prisms which melted at  $175^\circ$  [Found: Pt = 35.18.  $(C_2H_7N_3)_2, H_2PtCl_6$  requires Pt = 35.11 per cent.]. Schenck (*loc. cit.*) gives m. p.  $194$ — $195^\circ$  for the corresponding platinum salt prepared from methylguanidine obtained by the action of methylamine on *s*-methylthiocarbamide. The picrate, pale yellow, spherical



aggregates, decomposed at 285° without melting. The formation of methyldiguanide hydrochloride, as an intermediate product, in the above reaction was not considered of sufficient interest for further investigation.

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### CCXV.—Autoreduction of Sulphurous Acid.

By GEORGE MACDONALD BENNETT.

THE decomposition of sulphurous acid in aqueous solution has been repeatedly observed, but the reaction is usually a slow one unless fairly high temperatures are used. Thus dilute solutions of sulphur dioxide, exposed to sunlight for two months, yield sulphur and sulphuric acid (*Jahresber.*, 1873, 164). The reaction represented by the equation  $3\text{H}_2\text{SO}_3 = 2\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$  occurs when dilute solutions of sulphur dioxide are heated for several hours under high pressure in sealed tubes at 150–180° (Berthelot, *Ann. chim. phys.*, 1898, [vii], 14, 289).

The sulphites, bisulphites, and metabisulphites also undergo autoreduction when heated at 150–200°, with production of sulphur and a sulphate and sometimes the thiosulphate (Geuther, *Annalen*, 1884, 224, 218; Divers, T., 1885, 47, 205). It is explicitly stated by Barbaglia and Giucci (*Ber.*, 1880, 13, 2325) that the interaction of sulphur dioxide and a sulphite could not be detected during eight hours' heating at 140°.

The slow decomposition of sulphurous acid, which gives as ultimate products sulphur and sulphuric acid, was studied in greater detail by Jungfleisch and Brunel (*Compt. rend.*, 1913, 156, 1719). By sealing the solid hydrate in tubes, they attained concentrations of sulphur dioxide much higher than those in Berthelot's experiments. By this means the reaction was observed in the course of several days' heating at 100° or during longer periods at lower temperatures. Evidence was quoted to show that the yellow solution first produced in these experiments contained hyposulphurous acid,  $\text{H}_2\text{S}_2\text{O}_4$ , which then decomposed to give sulphuric acid and sulphur.

It has now been found that sulphurous acid, liberated in solution from its salts at temperatures of 100–120° or lower, may undergo instantaneous autoreduction with production of hydrogen sulphide. The reaction is best seen by dropping powdered sodium sulphite or metabisulphite, or saturated solutions of these salts, into hot aqueous sulphuric acid of 60–70 per cent. concentration, to which

a small quantity of antimonious oxide has previously been added. The orange sulphide appears immediately or on further heating. The antimony salt is not a catalyst necessary to the reaction, for it may be added afterwards or used to show the presence of hydrogen sulphide in the evolved gases by passing them over the moist oxide. Traces of the sulphides of mercury, lead, and copper are also obtained by sudden dilution of hot sulphuric or phosphoric acid solutions to which the oxide of the metal in question has been added and then solid sodium sulphite or metabisulphite.

This reaction may be assumed to follow the equation  $4\text{H}_2\text{SO}_3 = \text{H}_2\text{S} + 3\text{H}_2\text{SO}_4$ , corresponding to the change occurring when solid sodium sulphite is heated above  $150^\circ$ , namely,  $4\text{Na}_2\text{SO}_3 = \text{Na}_2\text{S} + 3\text{Na}_2\text{SO}_4$ .

It represents a possible intermediate stage in the liberation of free sulphur; this further reaction may, in fact, sometimes be observed in the above cases.

It appears, moreover, that this rapid autoreduction occurs only with sulphurous acid liberated from its salts, for all attempts to obtain it by using gaseous sulphur dioxide, saturated solutions, or the solid hydrate in place of the sulphites gave negative results. It seems possible that the high reducing power of the sulphurous acid under these conditions may be due to the momentary existence of the acid of the unsymmetrical formula,  $\text{H}\cdot\text{SO}_2\cdot\text{OH}$ , produced from a corresponding metallic salt such as was postulated by Divers and Shimidzu (T., 1886, 49, 577).

THE CHEMICAL DEPARTMENT,

GUY'S HOSPITAL MEDICAL SCHOOL, S.E. 1. [Received, July 19th, 1922.]

## CCXVI.—A Method for the Preparation of $\alpha\beta$ -Tri-alkylated Glutaric Acids.

By GEORGE ARMAND ROBERT KON and JOCELYN FIELD  
THORPE.

THE influence of substituents on the direction of the valencies of a carbon atom, particularly the effect of a *gem*-dialkyl grouping or a ring complex, has been the subject of a number of researches in these laboratories, and its great importance can scarcely be doubted. More recently (Kon, Stevenson, and Thorpe, this vol., p. 650), it was shown that an additional substituent in the  $\alpha$ -position can have a profound effect on the direction of the valencies and hence on the capacity of a substituted glutaric acid to pass into a cyclic structure. An examination of this effect is evidently of great

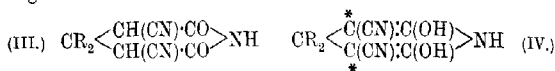
interest, but the difficulty of preparing suitable acids for investigation has, up to the present, made this impossible.

An attempt was therefore made to adapt Guareschi's method by which  $\beta\beta$ -disubstituted glutaric acids are usually prepared, using  $\alpha$ -cyanopropionic ester instead of cyanoacetic ester. It was hoped in this way to produce compounds of type I which on hydrolysis would yield  $\alpha\alpha\beta\beta$ -tetrasubstituted acids of type II:

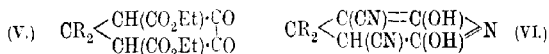


Unfortunately, it was only possible to obtain such a condensation product in one case, namely, that of *cyclohexanone*, and even in that instance the amount formed was so small as to render the method valueless for practical purposes. The work was therefore abandoned and the problem attacked from another direction.

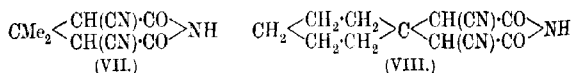
The condensation products of ketones with ethyl cyanoacetate and ammonia which serve as a source of  $\beta\beta$ -disubstituted glutaric acids and possess the general structure (III), were shown by Guareschi to behave as dibasic acids corresponding with a dienol form to which he (*Atti R. Accad. Sci. Torino*, 1901, [ii], 50, 235) assigned the formula IV rather than VI:



A consideration of a metallic derivative, such as the sodium compound, of this enol form (IV) reveals its great similarity with the sodium derivative of, for example, the diketopocamphoric ester (V) of Komppa, which, although it is strongly enolic in character,

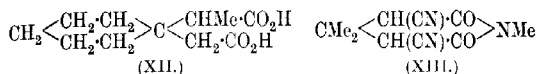
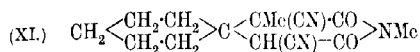
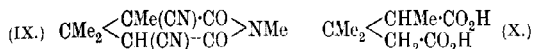


yet reacts, in the form of its sodium derivative, with methyl iodide yielding a methyl derivative having the methyl group attached to carbon (*Annalen*, 1909, 368, 126). It might therefore be expected that the sodium derivative of the dienol form (IV) would react with alkylating agents like methyl iodide and yield mono- and di-alkyl derivatives, having alkyl groups attached to the carbon atoms marked (\*), which would yield the desired acids on hydrolysis. The matter was tested experimentally, using the dicyanoinides (VII) and (VIII) as typical examples:

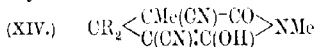


It was found that by the action of methyl iodide or methyl

sulphate in the presence of excess of sodium methoxide, dimethyl derivatives of these compounds could easily be prepared in good yield. On hydrolysing the new compounds, however, it was found that only one alkyl group was attached to carbon, since the *gem*-dimethyl compound (IX) yields  $\alpha\beta\beta$ -trimethylglutaric acid (X) and not  $\alpha\alpha\beta\beta$ -tetramethylglutaric acid on hydrolysis; similarly, the *cyclohexane* compound (XI) gives  $\alpha$ -methyl*cyclohexane*-1 : 1-diacetic acid (XII) :



It is possible readily to ascertain the position of the second entering alkyl group, which might, from the evidence afforded by hydrolysis, be attached either to nitrogen or to oxygen, because the compound (IX) is also formed on methylating the *N*-methyl derivative (XIII) obtained by Guareschi from acetone, ethyl cyanoacetate, and methylamine. It might therefore be concluded that formula VI in all probability represents the dienol form of Guareschi's cyanoimides, were it not for the remarkable fact that it appears to be impossible to destroy the acid nature of the dicyanoimides by alkylation with the ordinary reagents such as methyl iodide in the presence of sodium methoxide; the compounds retain one hydrogen with great tenacity. An attempt was made to replace this hydrogen by means of the usual etherifying agents such as alcohol and sulphuric acid, but without success, and therefore it must be concluded that the compound dialkylates in the form VI and that the remaining hydrogen then becomes enolic as in XIV and cannot be replaced by ordinary means, being the last mobile hydrogen atom of the tautomeric system.



For this reason, only  $\alpha$ -monosubstituted glutaric acids can be prepared by the method now described, but, owing to the easy manipulation and good yields obtained, the method should prove of considerable value. It appeared to be of interest to discover whether the first alkyl group to enter the molecule attaches itself to carbon or to nitrogen. For this purpose a few experiments were carried out using only one equivalent of sodium to one of imide. The evidence accumulated up to the present is rather inconclusive,

because the yields obtained under these conditions are poor and mixtures of compounds are produced. In the case of the *cyclohexane* compound (VIII) some of the *N*-methyl derivative was isolated in addition to the dimethyl compound, whilst the *gem*-dimethyl compound (VII) gave an equimolecular mixture of the *C*-methyl and the *N*-methyl derivatives mixed with a small quantity of the compound (IX). It is interesting to note, however, that when ethyl bromide was used as an alkylating agent, only *C*-mono-substitution products were obtained even with an excess of sodium ethoxide; the second ethyl group attaches itself to nitrogen, but can only be introduced with some difficulty.

#### EXPERIMENTAL.

The method adopted for the alkylation of the Guareschi compounds consists in dissolving sodium (1, 2, or 3 molecular proportions) in alcohol (methyl or ethyl), and adding the imide to the solution with vigorous shaking. An excess of the alkyl haloid is then added and the mixture boiled under reflux until neutral. It was found that the *cyclohexane* compound (VIII) was the most readily alkylated; the dimethyl compound (VII) required more time and was usually allowed to react over-night.

When the reaction is complete, the excess of alkyl haloid and the greater part of the alcohol are evaporated off, and the mixture is diluted with water and acidified with hydrochloric acid. The new imide usually separates in a solid form, otherwise rubbing with ether or alcohol is necessary to induce crystallisation.

Alkylation with methyl sulphate was found to work satisfactorily, although three molecular proportions of sodium methoxide have to be employed to obtain a good yield. An excess of methyl sulphate is very carefully added with constant shaking to the previously cooled solution of the imide in methyl-alcoholic sodium methoxide. The reaction is violent and is complete in a few minutes. It is then necessary to destroy the excess of methyl sulphate by rendering the now acid liquid alkaline with sodium hydroxide and warming until the addition of water no longer causes cloudiness. Most of the alcohol is then evaporated, water is added, and the liquid is acidified when cold. The yield of the new compound is almost theoretical. Unfortunately, it has not been found possible to use ethyl sulphate in the same way, as it was found to remain unchanged.

#### *Alkylation of the $\alpha$ -Imide of $\alpha\alpha'$ -Dicyano- $\beta\beta$ -dimethylglutaric Acid (VII).*

(1) *Monomethylation*.—The imide (15.2 grams) was treated with sodium methoxide (1 mol.) in about 60 c.c. of methyl alcohol, and

excess of methyl iodide. The crude product was obtained as a dark red oil, which solidified in contact with alcohol and was purified by spreading on porous porcelain. The yield of crude methylation product was about 50 per cent.

By recrystallisation from 95 per cent. alcohol the following compounds were isolated: (i) A small quantity (less than 1 gram) crystallising from methyl alcohol in spherical aggregates of fine, silky needles melting at  $143\text{--}144^\circ$ , identical with the dimethyl compound described below. (ii) A substance crystallising from ethyl alcohol in aggregates of thick prisms melting at  $129\text{--}130^\circ$ , and constituting the greater part of the reaction product. This, in spite of its definite properties, appears to be a mixture of the *C*- and *N*-methyl derivatives (Found:  $C = 58.51$ ;  $H = 5.65$ .  $C_{10}H_{11}O_2N_3$  requires  $C = 58.50$ ;  $H = 5.41$  per cent.), because on hydrolysis an equimolecular mixture of  $\alpha\beta$ -trimethyl- and  $\beta\beta$ -dimethyl-glutaric acids is obtained. So far the pure constituents have not been isolated.

(2) *Dimethylation*.—With two or, preferably, three molecular proportions of sodium methoxide and excess of methyl sulphate, the *N*-methyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha\beta\beta$ -trimethylglutaric acid (IX) is obtained in almost quantitative yield. After repeated crystallisation from methyl alcohol, this compound is obtained in spherical aggregates of fine, silky needles melting at  $143\text{--}144^\circ$  (Found:  $C = 60.45$ ;  $H = 6.06$ .  $C_{11}H_{13}O_2N_3$  requires  $C = 60.25$ ;  $H = 5.98$  per cent.).

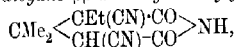
On attempting further methylation, the compound is recovered unchanged. It is also produced on methylation of the *N*-methyl imide (XIII) (p. 1797) with either methyl iodide or methyl sulphate.

The same compound is obtained in a different crystalline form, namely, in stout, hexagonal prisms melting about  $1^\circ$  higher, if the methylation is carried out by means of methyl iodide; the yield in this case is less satisfactory, being usually about 60 per cent. The compound has the same composition as the above (Found:  $C = 60.25$ ;  $H = 6.01$  per cent.), and an intimate mixture of the two melts at  $143\text{--}144^\circ$ . The solubility of the two forms is, however, different, the form crystallising in needles being the more soluble. A conversion of one form into the other ("seeding" of a saturated solution of one form with a crystal of the other) could not be achieved, but, on attempting to methylate the more soluble form by means of methyl iodide and sodium methoxide, the compound was recovered in the less soluble form.

On hydrolysis by means of sulphuric acid (Thole and Thorpe's method), both forms give a very good yield of  $\alpha\beta\beta$ -trimethylglutaric acid (X, p. 1797) which crystallises well from a mixture of benzene and

light petroleum (b. p. 60—80°) in transparent crystals belonging to the orthorhombic system, melting at 87—88° (Found: C = 55.49; H = 8.14. Calc., C = 55.15; H = 8.10 per cent.). The acid is identical with that obtained by Mr. K. C. Pandya of this College by Crossley's method (T., 1901, 79, 147) and readily gives the characteristic semianilide melting at 150°.

(3) *Monoethylation*.—The action of ethyl bromide in the presence of sodium ethoxide, even in large excess, on the imide causes the entrance of only one alkyl group and that is attached to carbon. The  $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid,



is obtained in about 80 per cent. yield (crude) and crystallises well from alcohol, forming sparkling, hexagonal plates melting at 207—208° (Found: C = 59.93; H = 5.98.  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3$  requires C = 60.25; H = 5.98 per cent.). This compound can be further ethylated by boiling its solution, in excess of alcoholic sodium ethoxide, with ethyl bromide for about eighteen hours. The product obtained is a mixture consisting of the original compound with a new substance, the latter predominating. The new compound, which is the *N*-ethyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid,  $\text{CMe}_2 \begin{array}{c} \text{<Cet(CN)·CO>} \\ \text{CH(CN)·CO} \end{array} \text{NEt}$ , can be separated

by repeated crystallisation from ethyl alcohol and is finally obtained in fine, rhombic plates melting at 113—114° (Found: C = 63.14; H = 7.15.  $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}_3$  requires C = 63.13; H = 6.92 per cent.).

On hydrolysis, a good yield of  $\alpha$ -ethyl- $\beta\beta$ -dimethylglutaric acid,  $\text{CO}_2\text{H}·\text{CHEt}·\text{CMe}_2·\text{CH}_2·\text{CO}_2\text{H}$ , is obtained from both the above compounds. The acid crystallises from a mixture of benzene and light petroleum (b. p. 60—80°) in aggregates of rhombic prisms melting at 112—113° (Found: C = 57.72; H = 8.65.  $\text{C}_9\text{H}_{16}\text{O}_4$  requires C = 57.41; H = 8.56 per cent.).

The *anhydride* was only obtained in the form of an oil; it was therefore converted into the *semianilide*, which readily solidified and separated from dilute alcohol in small, colourless needles melting at 136° (Found: C = 68.33; H = 8.14.  $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$  requires C = 68.39; H = 8.05 per cent.).

*Alkylation of the  $\omega$ -Imide of  $\alpha\alpha'$ -Dicyanocyclohexane-1 : 1-diacetic Acid (VIII).*

(1) *Monomethylation*.—This was carried out exactly as described in the case of the *gem*-dimethyl compound. The yield of methylation product was about 45 per cent.; the following compounds were isolated by repeated crystallisation from alcohol: (i) Slender

needles melting at  $175\text{--}176^\circ$  and forming about half of the original mixture. The compound is evidently Squintani's *N*-methyl derivative (*R. Accad. Sci. Torino*, 1912—13, 48, 675), as shown by analysis (Found: C = 63.62; H = 6.08. Calc., C = 63.67; H = 6.12 per cent.), and the formation of *cyclohexane-1:1*-diacetic acid on hydrolysis. (ii) Rhombic prisms, melting at  $164\text{--}165^\circ$ , consisting of the *N*-methyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -methylcyclohexane-1:1-diacetic acid (XI) identical with the dimethyl compound described below (Found: C = 64.96; H = 6.94.  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$  requires C = 64.83; H = 6.60 per cent.).

(2) *Dimethylation*.—This is best achieved by using a large excess of alcoholic sodium methoxide and methyl iodide, which leads to an almost theoretical yield of the new compound. Methyl sulphate can also be used, but a pure product is not usually obtained unless the methylation is repeated.

The methylation product consists of two substances, of which one occurs only in very small amount and sometimes not at all. This is readily separated, as it is insoluble in alkali; on crystallisation from alcohol, it forms small needles melting at  $212^\circ$  (Found: C = 74.22; H = 8.73; N = 10.81.  $\text{C}_{16}\text{H}_{22}\text{ON}_2$  requires C = 74.36; H = 8.60; N = 10.81 per cent.). The constitution of this substance has not yet been determined.

The second substance is the *N*-methyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -methylcyclohexane-1:1-diacetic acid (IX), which crystallises from methyl or ethyl alcohol in fine, colourless needles melting at  $166^\circ$  (Found: C = 64.80; H = 6.69; N = 16.57.  $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}_3$  requires C = 64.83; H = 6.60; N = 16.22 per cent.).

On hydrolysis with sulphuric acid, the imide yields  $\alpha$ -methylcyclohexane-1:1-diacetic acid (XII), which crystallises from a mixture of benzene and light petroleum (b. p.  $60\text{--}80^\circ$ ) or from dilute alcohol in hexagonal prisms melting at  $144\text{--}145^\circ$  (Found: C = 61.34; H = 8.52.  $\text{C}_{11}\text{H}_{18}\text{O}_4$  requires C = 61.65; H = 8.45 per cent.). The acid is far more soluble in benzene than the parent cyclohexanedi-acetic acid, which it resembles in other respects.

The *anhydride* of the acid is readily obtained in the usual way and crystallises from light petroleum (b. p.  $60\text{--}80^\circ$ ) in fine, iridescent needles melting at  $62^\circ$  (Found: C = 67.12; H = 8.16.  $\text{C}_{11}\text{H}_{16}\text{O}_3$  requires C = 67.21; H = 8.21 per cent.).

(3) *Monoethylation*.—The operation is carried out in the same way as with the *gem*-dimethyl compound (see p. 1800), using two molecular proportions of sodium ethoxide; a good yield of the new compound is obtained. The main product is accompanied by a very small amount of a neutral substance crystallising in small needles, melting at  $205^\circ$ , doubtless analogous to the by-product



obtained in the methylation of the imide (VIII) (see p. 1801). The main product crystallises from alcohol, in which it is rather sparingly soluble, in silvery plates melting at  $226-228^\circ$ , but the melting point is not quite sharp. It is the  $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -ethylcyclohexane-1:1-diacetic acid,  $C_5H_{10}:C \begin{smallmatrix} \text{C} \text{Et}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{smallmatrix} > \text{NH}$  (Found: C = 64.52; H = 6.80.  $C_{14}H_{17}O_2N_3$  requires C = 64.83; H = 6.60 per cent.).

Further ethylation of this compound proceeds with some difficulty and leads to the formation of the *N*-ethyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -ethylcyclohexane-1:1-diacetic acid,  $C_5H_{10}:C \begin{smallmatrix} \text{C} \text{Et}(\text{CN}) \cdot \text{CO} \\ \text{CH}(\text{CN}) \cdot \text{CO} \end{smallmatrix} > \text{NEt}$ , which forms fine, silky, flattened needles, melting at  $163.5^\circ$  after repeated crystallisation from alcohol. It is more soluble in alcohol than the preceding compound (Found: C = 66.42; H = 7.47.  $C_{16}H_{21}O_2N_3$  requires C = 66.84; H = 7.38 per cent.).

Both the above compounds, on hydrolysis with sulphuric acid, give the same  $\alpha$ -ethylcyclohexane-1:1-diacetic acid,  $C_5H_{10}:C \begin{smallmatrix} \text{CH} \text{Et} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , which crystallises from dilute alcohol in elongated prisms melting at  $187^\circ$ . It appears to be almost insoluble in benzene (Found: C = 62.92; H = 8.80.  $C_{13}H_{20}O_4$  requires C = 63.11; H = 8.85 per cent.). The anhydride and semianilide were prepared, but could not be obtained in a crystalline form.

*Condensation of cyclohexanone and Ethyl  $\alpha$ -Cyanopropionate.*—5.4 Grams of cyclohexanone were condensed with 14 grams of the ester, using the method previously described (Kon and Thorpe, T., 1919, 115, 693). After forty-eight hours' standing, the liquid had deposited colourless crystals (0.75 gram), which were not the expected ammonium salt. These were collected and purified by crystallisation from alcohol or acetic acid, being obtained from the latter in fern-like aggregates of prisms melting at  $249^\circ$ . The empirical formula of the substance appears to be  $C_{15}H_{20}ON_2$  (Found: C = 73.65; H = 8.34; N = 11.80.  $C_{15}H_{20}ON_2$  requires C = 73.70; H = 8.27; N = 11.47 per cent.), but its constitution has not yet been elucidated.

On diluting and acidifying, the liquid reaction mixture deposited a small amount (about 1 gram) of a white, crystalline solid after standing for several days; in some experiments none was obtained. The substance formed a microcrystalline powder melting at  $180-182^\circ$  and consisted of the  $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha\alpha'$ -dimethylcyclohexane-1:1-diacetic acid,  $C_5H_{10}:C \begin{smallmatrix} \text{C} \text{Me}(\text{CN}) \cdot \text{CO} \\ \text{C} \text{Me}(\text{CN}) \cdot \text{CO} \end{smallmatrix} > \text{NH}$  (Found: C = 64.75; H = 6.60; N = 16.48.  $C_{14}H_{17}O_2N_3$  requires C = 64.83; H = 6.60; N = 16.22 per cent.).

The action of cold concentrated sulphuric acid on this imide leads, as in other similar cases (see Kon and Thorpe, *loc. cit.*, p. 694), to the formation of the  $\omega$ -imide of  $\alpha\alpha'$ -dicarbamyl- $\alpha\alpha'$ -dimethylecyclohexane-1:1-diacetic acid,  $C_6H_{10} \cdot C \begin{smallmatrix} \text{CMe}(\text{CO} \cdot \text{NH}_2) \cdot \text{CO} \\ \text{CMe}(\text{CO} \cdot \text{NH}_2) \cdot \text{CO} \end{smallmatrix} > \text{NH}$ , which forms a highly insoluble, microcrystalline powder which can be recrystallised from a large quantity of glacial acetic acid and melts with decomposition at  $270-271^\circ$  (Found: C = 56.85; H = 7.20; N = 14.30.  $C_{14}H_{21}O_4N_3$  requires C = 56.98; H = 7.12; N = 14.24 per cent.). The non-nitrogenous acid was not prepared owing to lack of material.

The experiments described in the last section were carried out by Mr. W. H. Gough, M.Sc., to whom our thanks are due.

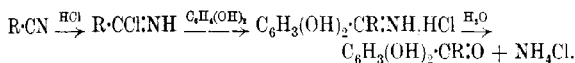
THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON.

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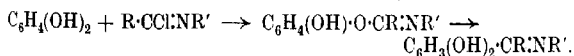
### CCXVII.—*The Condensation of Phenols with the Hydrochlorides of Cyanamides and Carbodi-imides, and its Relation to the Hoesch Reaction.*

By WALLACE FRANK SHORT and JOHN CHARLES SMITH.

THE reactions involved in Hoesch's method (*Ber.*, 1915, **48**, 1122) for the preparation of aromatic hydroxy-ketones were assumed by its author to be the following:

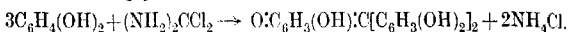


Evidence in support of such a series of reactions has been brought forward by Stephen (T., 1920, **117**, 1529), who showed that the  $\omega$ -chlororesacetophenone,  $C_6H_3(OH)_2 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , obtained by Sonn (*Ber.*, 1917, **50**, 1262) by condensing chloroacetonitrile with resorcinol according to Hoesch's method, can also be obtained by warming chloroacetimide chloride,  $\text{CH}_2\text{Cl} \cdot \text{CCl} \cdot \text{NH}$ , with resorcinol. In a similar manner, Stephen condensed certain *N*-substituted iminochlorides with resorcinol and obtained the anils of the corresponding hydroxy-ketones, and has suggested the formation of an intermediate imino-ether which subsequently changes into the anil:



It seemed desirable to determine whether the introduction of a

basic group into the nitrile or *N*-substituted imino-chloride would change the nature of its reaction with phenols. The derivatives of cyanamide and of the hypothetical chloroformamidine,  $\text{H}_2\text{N}\cdot\text{CCl}\cdot\text{NH}$ , were chosen for this investigation because, if these behaved in a normal manner, a new method for the preparation of substituted benzamidines would have resulted. The condensation of cyanamide itself with resorcinol by the Hoesch method leads to the precipitation of cyanamide dihydrochloride, which slowly reacts with the resorcinol to produce a small quantity of resaurin. The same product is obtained by fusing together cyanamide dihydrochloride and resorcinol. This result leads to  $\text{NH}_2\cdot\text{CCl}_2\cdot\text{NH}_2$  as the most probable formula for cyanamide dihydrochloride, the reaction taking place according to the equation

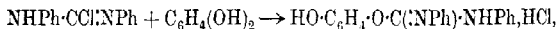


Further, it seems reasonable to suppose that the small quantity of highly coloured by-product frequently obtained in the Hoesch reaction is an aurin produced in the same way.

Attempts to prepare cyanamide monohydrochloride were not successful, and the condensation of a mixture of cyanamide dihydrochloride (0.5 mol.) and cyanamide (0.5 mol.) with sodium phenoxide (1 mol.) did not lead to the production of the phenyl ether of isocarbamide, but to the regeneration of phenol and formation of dicyanodiamide.

Although it is stated in the literature (compare Beilstein's "Handbuch der organischen Chemie") that the substituted cyanamides do not unite with hydrogen chloride, we have found that dibenzylcyanamide forms a stable dihydrochloride, which also condenses with resorcinol to produce resaurin.

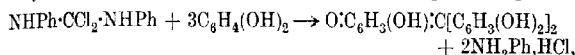
The condensation of carbodiphenylimide monohydrochloride with phenols by gentle warming leads to the production of ethers of diphenylisocarbamide. These substances have been prepared by Busch, Blume, and Pungs (*J. pr. Chem.*, 1909, [ii], **79**, 513) by the condensation of phenols with carbodiphenylimide at a relatively high temperature. Since the maximum yield of ethers is obtained by employing one equivalent of hydrogen chloride, it is evident that the monohydrochloride of carbodiphenylimide is involved,



and the reaction supports the suggestion made by Stephen (*loc. cit.*). At the same time, attempts to cause the *O*-ethers to undergo isomeric change, with migration of the  $\cdot\text{C}(\text{NPh})\cdot\text{NHPh}$  group into the nucleus in the ortho- or para-position, were unsuccessful. That this is due to the introduction of an additional basic group into the

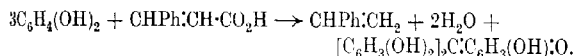
molecule seems probable from the fact that the *p*-nitrophenyl ether of diphenylisocarbamide undergoes a different isomeric change, into *p*-nitrotriphenylcarbamide.

At higher temperatures, resorcinol condenses with carbodiphenylimide monohydrochloride to produce resaurin. Since the *m*-hydroxyphenyl ether of diphenylisocarbamide, produced by the interaction of resorcinol and carbodiphenylimide monohydrochloride at lower temperatures, does not condense with resorcinol to produce resaurin, it seems clear that the production of the latter is due to the formation of carbodiphenylimide dihydrochloride. This conclusion is confirmed by the fact that carbodiphenylimide dihydrochloride condenses with resorcinol according to the equation



and the constitution of the dihydrochloride is at the same time elucidated.

It is interesting to note that phenol, which does not give the Hoesch reaction, is also incapable of producing aurins, although it gives rise to others. At the same time, it has been found that whereas resorcinol yields resaurin on fusion with potassium hydrogen carbonate, phenol does not give rise to aurin. As a result of this observation, it is possible to explain the reaction which takes place on fusing cinnamic acid with resorcinol and anhydrous zinc chloride. Bargellini and Marantonio (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 119) state that the product of this reaction is 2:4-dihydroxyphenyl styryl ketone. Stephen (*loc. cit.*) failed to obtain a trace of this ketone, but observed that the product consisted of a red substance, which he did not examine further. The red product contains resaurin, and styrene is simultaneously liberated.



#### EXPERIMENTAL.

*Cyanamide Dihydrochloride and Resorcinol.*—By passing dry hydrogen chloride into a solution of resorcinol and cyanamide in anhydrous ether, with or without addition of anhydrous zinc chloride, cyanamide dihydrochloride is precipitated; a small quantity of resaurin may be obtained from the solution.

A mixture of cyanamide (1 mol.) and resorcinol (3 mols.) was heated at 170° for three hours, and the product extracted with water; ammonium chloride and dicyanodiamide were obtained from the solution, and the residue consisted of resaurin. The last substance has been briefly described by Nencki and Sieber

(*J. pr. Chem.*, 1881, [ii], **23**, 547). It is a brick-red, hygroscopic solid, slightly soluble in water, easily soluble in methyl or ethyl alcohol or acetone, moderately soluble in ethyl acetate or ether, and practically insoluble in chloroform, light petroleum, benzene, or toluene. It is easily soluble in sodium carbonate, but much less soluble in sodium hydrogen carbonate. In alkaline solution, it has a beautiful dark red colour. Dilute solutions exhibit an intense green fluorescence, especially in the presence of a trace of ammonia. On heating, it does not melt, but darkens between 230° and 240°, apparently with some decomposition. No acetyl or benzoyl derivative could be obtained. For this reason, the production of resaurin in all the reactions mentioned in this paper was confirmed by carrying out an analysis of the red substance after purification by repeated crystallisation from dilute alcohol and drying at 110°.

*Dibenzylcyanamide Dihydrochloride*.—Three grams of dibenzylcyanamide, dissolved in 10 c.c. of anhydrous ether, were treated with a current of dry hydrogen chloride for two minutes. If the stream of hydrogen chloride is continued, the faintly coloured oil precipitated will be redissolved and can only be recovered by the addition of a large volume of ether. The oil soon crystallises and is then washed with ether. Colourless cubes, melting at 130–133° with slight decomposition, are obtained (Found: Cl = 24.0, 23.8; N = 9.54.  $C_{15}H_{14}N_2 \cdot 2HCl$  requires Cl = 24.07; N = 9.49 per cent.). Dibenzylcyanamide dihydrochloride is decomposed by cold water into its constituents. It may also be obtained by passing dry hydrogen chloride into the molten cyanamide, in an atmosphere of the same gas.

*Dibenzylcyanamide and Resorcinol*.—Resorcinol (11 grams; 3 mols.) was dissolved in dry ether (100 c.c.) and dibenzylcyanamide (7.4 grams; 1 mol.) added. A current of dry hydrogen chloride produced a heavy, red, oily layer, which was extracted with water and cold dilute sodium hydroxide. The aqueous extract was concentrated in a vacuum and treated with strong caustic soda solution. Ammonia was evolved and a small quantity of light oil separated. The latter was taken up in ether and the dry solution divided into two parts. The first was treated with a current of dry hydrogen chloride; the white precipitate thus obtained melted at 256° after recrystallisation from absolute alcohol. Paal and Gerum (*Ber.*, 1909, **42**, 1557) state that dibenzylamine hydrochloride melts at 257–258°. The ether was removed from the second portion of the solution, and the residue acetylated by the Schotten-Baumann method. The purified acetyl derivative melted at 93° (Found: N = 6.00.  $C_{16}H_{17}ON$  requires N = 5.86 per cent.).

The alkaline extract, on acidification, yielded a small quantity of resaurin (Found: C = 66.95; H = 4.20 per cent.).

Examination of the residue insoluble in water and sodium hydroxide showed that it consisted of dibenzyleyanamide.

The same products were obtained by warming dibenzyleyanamide dihydrochloride with resorcinol.

*The Condensation of Carbodiphenylimide Monohydrochloride with Phenols.*—The preparation of pure carbodiphenylimide monohydrochloride (Stieglitz and Lengfeld, *Amer. Chem. J.*, 1895, **17**, 98) is an extremely tedious operation. Fortunately, the isolation of this substance proved to be unnecessary, since the use of a reaction mixture containing one equivalent of hydrogen chloride was found to give the same results as the pure hydrochloride. Since the phenyl ethers of diphenylisocarbamide have already been described (Busch, Blume, and Pungs, *loc. cit.*), the following is sufficient to illustrate the mode of procedure.

*Phenyl Ether of isoDiphenylcarbamide*,  $C_6H_5 \cdot O \cdot C(XPh) \cdot NHPh$ .— $\alpha$ -Carbodiphenylimide (9.7 grams; 1 mol.) was dissolved in 80 c.c. of dry benzene and treated with dry hydrogen chloride until the increase in weight amounted to 1.8 grams (1 mol.). Phenol (4.7 grams; 1 mol.) was added, the solvent removed under diminished pressure, and the residue heated for five minutes at a temperature slightly above its setting-point. When cold, the product was neutralised with 5 per cent. alcoholic sodium hydroxide, and in this way 12 grams of the phenyl ether of diphenylisocarbamide (m. p. 104–105°) were obtained from the alcoholic solution.

The *p*-tolyl and  $\beta$ -naphthyl ethers of diphenylisocarbamide were similarly prepared and were found to have the properties described by Busch, Blume, and Pungs (*loc. cit.*). The *p*-nitrophenyl ether, however, was found to melt at 105° and not at 100°, as given by these authors; its conversion into *p*-nitrotriphenylcarbamide was confirmed by heating a pure sample at 160°.

*Carbodiphenylimide Monohydrochloride and Resorcinol.*—The *m*-hydroxyphenyl ether of diphenylisocarbamide was obtained in the same way by heating the reactants at 100° for a short time. The yield was 80 per cent. of the theoretical, and the product identical with that obtained by Busch, Blume, and Pungs; no  $\gamma$ -carbodiphenylimide was formed as by-product in our preparation.

On condensing carbodiphenylimide monohydrochloride with resorcinol at 130°, a dark red, viscous oil was obtained, which proved to consist of a mixture of the *O*-ether, carbodiphenylimide, aniline hydrochloride, and resaurin.

*Carbodiphenylimide Dihydrochloride and Resorcinol.*—Carbodiphenylimide dihydrochloride (6.7 grams; 1 mol.) was treated with

a solution of 8.3 grams (1 mol.) of resorcinol in ether (50 c.c.); the solvent was then removed and the residue maintained at  $130^{\circ}$  for an hour. When cold, the product was rendered alkaline with dilute sodium hydroxide and distilled in a current of steam. The oily distillate was shown to be aniline, whilst resaurin was precipitated from the residue by acidification with hydrochloric acid.

*Cinnamic Acid and Resorcinol.*—Resorcinol (16.5 grams; 3 mols.) was mixed with cinnamic acid (7.4 grams; 1 mol.) together with powdered zinc chloride (3 grams), and the mixture slowly heated to  $160^{\circ}$  in an oil-bath. The dark red mass evolved steam containing a small quantity of an oil, which was identified as styrene by bromination (styrene dibromide, m. p.  $74^{\circ}$ ). The residue contained resaurin, but no trace of 2:4-dihydroxyphenyl styryl ketone could be detected.

The authors desire to thank Professor Worley for facilities placed at their disposal in connexion with this investigation.

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# CCXVIII.—*The Mathematics of the Dicyclic Colour Theory, and a New Theory of the Structure of the Nitrogen Atom.*

By JAMES MOIR.

LAST year the author put forward the conception that the cause of colour in a "dicyclic" substance is the performance of an oval orbit by an electron going round the whole molecule (T., 1921, 119, 1637). The time of revolution of the electron was taken to be identical with the time required for light to travel over a length equal to the absorption wave-length of the coloured substance.

Professor W. N. Roseveare of Pietermaritzburg now supplies the following mathematical investigation of the problem, whereby it is shown, using the ordinary laws of dynamics, that an electron attracted by two equal positive nuclei can describe a certain elliptic orbit having its foci at the nuclei. The electron must cross the line of foci at right angles and with a velocity which is prescribed in terms of its distance,  $s$ , at that moment from the nuclei.

Professor Roseveare also obtains a formula for calculating the periodic time of revolution in the orbit in terms of the focal (inter-





Hence, comparing (i) and (iii), we have  $K = 1/a$ , whence from (ii) we have

$$\frac{u^2}{2\mu} = \frac{2a}{b^2} - \frac{1}{a} = \frac{1}{a} \cdot \frac{1+e^2}{1-e^2} \quad \dots \quad (iv)$$

This equation gives the eccentricity of the ellipse in terms of the initial velocity and the distance of the electron from the mid-point of the positive forces. The latter,  $a$ , is probably practically constant, since the electron must pass close to the auxochrome groups, and the eccentricity is also consequently high, and probably constant—according to the quantum theory necessarily confined to a set of constant values, all probably high.

The time of revolution is calculated as follows:

Equation (iii) for the velocity at any point is rewritten with the substitutions  $x = a \cos \phi$  and  $y = b \sin \phi$ ,  $V$  being  $\frac{ds}{dt}$ .

$$\begin{aligned} \text{Then } (a^2 \sin^2 \phi + b^2 \cos^2 \phi) \left( \frac{d\phi}{dt} \right)^2 &= \frac{2\mu}{a} \left( \frac{2a^2}{b^2} - 1 \right) \\ &= \frac{2\mu}{a} \left( \frac{2a^2 - (a^2 \sin^2 \phi + b^2 \cos^2 \phi)}{a^2 \sin^2 \phi + b^2 \cos^2 \phi} \right) \end{aligned}$$

Hence, putting  $c^2$  for  $a^2 - b^2$ ,

$$\sqrt{\frac{2\mu}{a}} dt = \frac{a^2 \sin^2 \phi + b^2 \cos^2 \phi}{\sqrt{a^2 + c^2 \cos^2 \phi}} d\phi,$$

$$\text{or } \sqrt{\frac{2\mu}{a}} dt = a (1 - e^2 \cos^2 \phi) (1 + e^2 \cos^2 \phi)^{-\frac{1}{2}} d\phi.$$

Hence, by integration,

$$T \sqrt{\frac{2\mu}{a}} = \int_0^{2\pi} d\phi \sum_{n=0}^{\infty} e^{2n} \cos^{2n} \phi [C_n - C_{n-1}],$$

$$\text{when } C_n = (-)^n \frac{1 \cdot 3 \cdot 5 \dots 2n-1}{2 \cdot 4 \cdot 6 \dots 2n}.$$

$$\begin{aligned} \text{Thus, since } \int_0^{\pi/2} \cos^{2n} \phi d\phi &= \frac{\pi}{2} C_n, \\ \text{we have } T \sqrt{\frac{2\mu}{a^3}} &= (-)^n \sum e^{2n} 2\pi C_n^2 \left( 1 + \frac{2n}{2n-1} \right) \\ &= 2\pi \left[ 1 - \frac{3}{1} \left( \frac{1}{2} \right)^2 e^2 + \frac{7}{3} \left( \frac{1 \cdot 3}{2 \cdot 4} \right)^2 e^4 - \frac{11}{5} \left( \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6} \right)^2 e^6 + \text{etc.} \right] \end{aligned}$$

The series on the right is convergent and, when the eccentricity is given, can be evaluated numerically (for example, when  $e = \frac{2}{3}$ , the series =  $1.4342 \pi$ ).

Thus we have the important result that the periodic time, as in simple elliptic orbits round *one* nucleus, is proportional to the

three-halves power of the length of the major axis of the ellipse, that is,  $T = ka^{3/2}$ , and when the eccentricity is practically prescribed by the auxochrome, the periodic time is proportional to  $c^{3/2}$ , since  $c = ae$ .

*Explanation of the Colour Factors.*

In the paper quoted, the linkage-factors for methylene-, imino-, oxo-, and thio-groups were given as respectively 0.65, 0.78, 0.891, and 0.92.

Now according to the present mathematical theory these four figures must be in the ratio of the four periodic times of revolution in the four different ellipses associated with the four prototype coloured substances [for example, dihydroxybenzhydrol, dihydroxy-diphenylhydroxylamine indophenol], and the corresponding peroxides and sulfoxides].

Therefore, from the foregoing theory we can find the ratio of the sizes of the ellipses (the ratios between their major axes) by extracting the two-thirds root of the four colour factors. The results are respectively 0.750, 0.847, 0.926, and 0.946.

The value unity now belongs to the imaginary major axis of an orbit going round two phenoxide-rings side by side, to which the vibration  $\lambda$  1380 was assigned in the first paper of this series. To eliminate this imaginary factor we multiply the above four figures by  $(1 \div 0.926)$ , thus making the oxygen compound the standard one.

The sizes of the four ellipses are then 0.810, 0.915, 1.000, and 1.021.

I now suggest a simple physical explanation of these figures, namely (1) that in the oxo-compound the molecule is in one straight line ( $A-C_6H_4-O-C_6H_4-A'$ ); (2) that in the methylene compound the two halves of the molecule lie at the angle governed by the

carbon tetrahedron ( $109.4^\circ$ )  $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\ \text{A} \quad \text{A}' \end{array}$ ; (3) that in the

imino compound the angle between the benzene rings is  $133^\circ$  when the compound is exhibiting its chief absorption band, and is (probably)  $120^\circ$  and  $107^\circ$  for subsidiary bands.

The distance between  $A$  and  $A'$  in the methylene compound is related to the distance between  $A$  and  $A'$  in the oxo-compound by a ratio which is the sine of half the angle of deviation, assuming that the carbon atom is only very slightly different in size from the oxygen atom. Now the sine of  $109.4^\circ/2$  is just greater than the figure 0.81 found above for the methylene compound. If the oxygen atom is about 5 per cent. wider than the methylene-carbon

atom, the ratio of the distances  $Ad'$  in the two cases is exactly 0.81, using the tetrahedral angle of  $109.4^\circ$ .

This being established, we can employ the colour data to find the hitherto unknown angle between the valencies of tervalent nitrogen. The fraction 0.915 is the sine of half the required angle, which is  $132^\circ$ . This becomes  $133^\circ$  if we assume the nitrogen atom to be intermediate in diameter between carbon and oxygen. This result is quite different from the angle assumed in the Hantzsch-Werner hypothesis ( $109^\circ$ ) and is also larger than the angle ( $120^\circ$ ) resulting from three equal plane valencies; but I do not think there is any evidence against the conception of three *unequal plane* valencies, the different combinations of which would explain the isomerism of the oximes, and would not involve the very definite asymmetry in the compounds  $Nabc$  which the Hantzsch-Werner hypothesis requires.

Now most of the phenazines, phenoxazines, and phenthiazines exhibit two bands at once in their spectrum. If this really connotes two simultaneous or alternative orbits, we can employ the measurements of the subsidiary bands to calculate the other angle (or angles) between the valencies of nitrogen. The imino-linkage colour-factor for this lower band is about 0.72 (that of the main band being 0.78). The two-thirds root of 0.72 is 0.80, and  $0.80 \div 0.926 = 0.86$ . This is therefore the sine of half the required angle, which is  $120^\circ$  when corrected for the size of the nitrogen atom compared with oxygen.

We thus obtain  $133^\circ$  and  $120^\circ$  as the angles between two pairs of valencies in tervalent nitrogen. If the valencies are plane, the remaining angle is  $360^\circ - 253^\circ$  or  $107^\circ$ . If they are not plane, the third angle is smaller than this.

As regards the thio-compounds, of size 1.021, I suggest that they are straight like the oxo-compounds, and that the 2.1 per cent. difference is merely due to the larger diameter of the sulphur atom, which is known to have two octets of electrons instead of the one possessed by carbon, nitrogen, and oxygen.

#### Summary.

- (a) The oxo-colour-factor 0.891 is  $\left(0.926 \sin \frac{180^\circ}{2}\right)^{2.2}$ .
- (b) The two imino-factors, 0.78 and 0.72, are respectively  $\left(0.926 \sin \frac{133^\circ.22}{2}\right)$  and  $\left(0.926 \sin \frac{120^\circ.22}{2}\right)$ , with a small correction for the smaller size of the nitrogen atom.
- (c) The methylene-factor 0.65 is  $\left(0.926 \sin \frac{109.4^\circ}{2}\right)^{2.2}$  with an analogous small correction.

(d) The factor 0.926 is apparently the ratio of the size of the molecule of dihydroxydiphenyl oxide to the size of two juxtaposed molecules of phenol (both substances supposed ionised) and represents the contraction on replacing two para-hydrogen atoms by the oxo-linking.

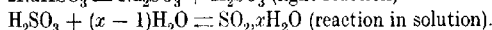
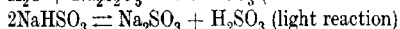
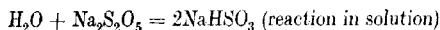
GOVERNMENT LABORATORY,  
HOSPITAL STREET, JOHANNESBURG.

[Received, May 16th, 1922.]

### CCXIX.—*The Equilibria in Aqueous Solutions of the Alkali Metal Bisulphites.*

By EDWARD CHARLES CYRIL BALY and ROBERT ARTHUR BAILEY.

THE conditions which exist in aqueous solutions of the alkali metal bisulphites have been investigated by several observers, chiefly by spectrographic methods, but no satisfactory conclusions have been drawn. Wright (T., 1914, 105, 2909) investigated the absorption spectra of aqueous solutions of sulphur dioxide and of the normal sulphites, and he concluded that the former contain a large proportion of uncombined molecules of sulphur dioxide, since the absorption curves are similar to those exhibited by the gas. Garrett (T., 1915, 107, 1324) found that aqueous solutions of sulphur dioxide, when half neutralised by rubidium, potassium, sodium, or ammonium hydroxide, showed no selective absorption, but that after these solutions were allowed to remain in the light an absorption band appeared at  $\lambda = 276 \mu\mu$ , the maximum absorptive power being developed in about twenty-eight days. Since the same phenomenon was shown by solutions of the meta-bisulphites, he drew the conclusion that on exposure to light an equilibrium was established:



Although the absorption band was identical in position with that shown by aqueous solutions of sulphur dioxide, the absorptive power of solutions of equal concentration varied with the metallic radicle, and was always much smaller than that of the free acid. The phenomenon was not observed with the bisulphite solutions when these were protected from light. Schaeffer and his co-workers (Z. Elektrochem., 1915, 21, 181; Z. anorg. Chem., 1918, 104, 212) also observed this time phenomenon and further found that selective absorption is shown both by freshly prepared solutions of

potassium metabisulphite and by solutions of sodium sulphite containing one equivalent of sulphuric acid. Since he found no selective absorption with half-neutralised solutions of sulphur dioxide, he considered that the end-point had been reached immediately. He concluded that the selective absorption initially shown is due to an isomeric form of the bisulphite molecule.

In an investigation of the additive compounds formed by sodium and potassium bisulphites we have found it necessary to reopen the question, and the results obtained would seem to afford an explanation of the conditions which exist in these solutions. In the following account of our results the absorptive power is expressed in terms of the molecular extinction coefficient, which is given by  $\log(I_0/I) \times 1/CD$ , where  $I_0/I$  is the ratio of intensity of the incident and the transmitted light,  $C$  is the concentration in gram-molecules per litre, and  $D$  is the thickness in centimetres of the solution employed.

We first investigated the absorption spectra of solutions of sulphur dioxide which had been prepared with water free from carbon dioxide and then half neutralised by sodium, potassium, or rubidium hydroxide. In each case the freshly prepared solution exhibited an absorption band at  $\lambda = 257 \mu\mu$  and this band was also shown by a freshly prepared solution of potassium metabisulphite. On exposing these solutions in stoppered flasks to light, it was found that this absorption band disappeared, its place being taken by a second band at  $\lambda = 276 \mu\mu$ , the change being accompanied by a marked increase in the absorptive power. The velocity of this change increases very materially with dilution, since in the case of very dilute solutions it takes place even in the dark, whilst with a 0.25 *M*-solution it is incomplete even after many days, a broadening of the band towards the red only being observed. It seems probable, therefore, that the phenomenon is due to an ionic reaction of some kind, very possibly oxidation.

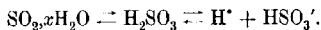
This explanation receives support from the results obtained by Matthews and his co-workers (*J. Physical Chem.*, 1913, 17, 211; *J. Amer. Chem. Soc.*, 1917, 39, 635) in their experiments on the photo-oxidation of sodium sulphite in solution. They found that benzaldehyde, phenol, and pyridine act as very efficient negative catalysts in this reaction, but we were unable to employ this method owing to the powerful selective absorption exerted by these substances. We have, however, proved that the change is due to oxidation by the use of solutions from which air was entirely excluded. 0.1, 0.05, and 0.025 *M*-Solutions were made of potassium metabisulphite in air-free water, and these were divided into two portions. Stoppered bottles were completely filled with the one

portion and after the stopper had been inserted it was covered with paraffin wax. The other portion was placed in stoppered flasks containing some air, and both bottles and flasks were exposed to light. After the lapse of several days the bottles and flasks were opened and their contents titrated against a standard iodine solution. When the three solutions were first made up, 25 c.c. of the iodine solution required 16.84, 33.70, and 67.40 c.c., respectively, of the three solutions, and the following table shows the titration values after stated periods of time, 25 c.c. of the iodine solution being used in each case.

Concentration.	Time in days.	Titre of solution in sealed bottles.	Titre of solution in flasks.
0.1M	10	16.85 c.c.	23.00 c.c.
	26	16.85 "	
0.05M	8	33.67 "	45.62 "
	25	33.72 "	
0.025M	6	67.51 "	110.4 "
	25	67.49 "	

The absorption spectra of the solutions were observed at the same time as the titrations were made, and the curves obtained for the 0.1M-solutions are shown in Fig. 1. Whereas no change was noted in the case of the air-free solutions, the change in the position of the absorption band exhibited by the aerated solution is well marked, together with the increase in molecular extinction from 27.3 to 72.5. In the case of the 0.025M-solutions, after six days' exposure to light, the absorption curve of the oxidised portion approximates to that of a mixture of equal volumes of 0.05M-potassium sulphate and 0.05M-sulphur dioxide solutions. It is obvious therefore that the time reaction consists in the photo-oxidation of the  $\text{HSO}_3'$  ion.

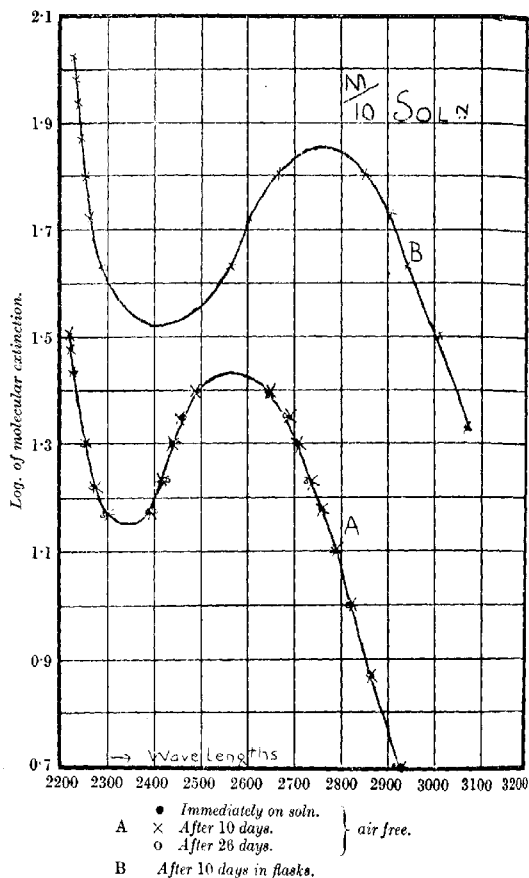
There still remains to be explained the absorption band at  $\lambda = 257 \mu\mu$ , and we have succeeded in finding the origin of this band by a comparison of the absorptive power with the concentration of the constituents as determined by conductivity measurements. In order to prove that this method of comparison is trustworthy, we first of all determined the two sets of data for aqueous solutions of sulphur dioxide, in which case the following equilibrium exists:



Since the concentration of  $\text{SO}_2 \cdot x\text{H}_2\text{O}$  is directly proportional to the concentration of  $\text{H}_2\text{SO}_3$ , it is proportional to the total amount of sulphur dioxide present in the non-ionised condition. The latter can be determined from the conductivity measurements made by Lindner (*Monatsh.*, 1912, **33**, 613), and hence the concentration of  $\text{SO}_2 \cdot x\text{H}_2\text{O}$  may be assumed to be proportional to the

difference between the molecular conductivity at infinite dilution (398) and the molecular conductivity at the dilution required. The proportional concentration of  $\text{SO}_2 \cdot x\text{H}_2\text{O}$  as determined from

FIG. 1.

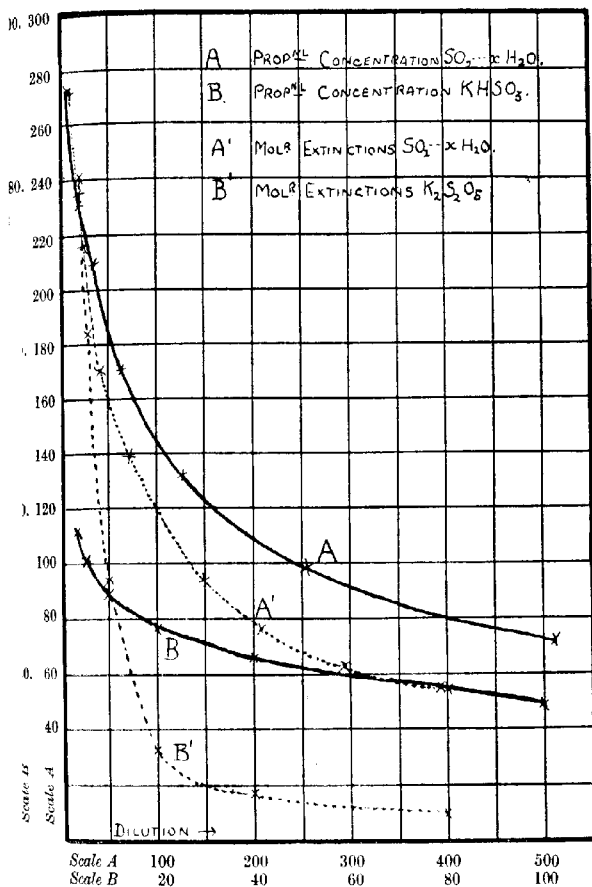


conductivity and spectrographic measurements can thus be compared, and the two curves, A and A', are shown in Fig. 2. The similarity in type between these two curves justifies us in using the same method to determine whether the absorption band at

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 AQUEOUS SOLUTIONS OF THE ALKALI METAL BISULPHITES.

$\lambda = 257 \mu\mu$ , shown by freshly prepared solutions of potassium metabisulphite, is due to the  $\text{KHSO}_3$  molecule. Barth's values for the conductivity of potassium hydrogen sulphite solutions were

FIG. 2.



used (*Z. physikal. Chem.*, 1892, 9, 176), but since these did not extend to greater concentrations than  $M/32$ , we extended them to as far as the concentration  $M/10$ . The value of  $\Lambda_\infty$  was taken as 126.79, and the conductivity and spectrographic measurements



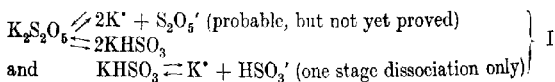
are shown by the curves *B* and *B'* in Fig. 2. The marked difference in type between these two curves proves that the absorption band at  $\lambda = 257 \mu\mu$  is not due to potassium hydrogen sulphite.

On the other hand, the extinction coefficient,  $\log(I_0/I) \times 1/D$ , which is a measure of the actual concentration of the absorbing substance, was found in the case of potassium metabisulphite solutions to decrease to rather less than one-fourth when the concentration was reduced to one-half. The actual values obtained were as follow:

Concentration .....	0.5	0.25	0.1	0.05	0.025 <i>M</i>
Extinction coefficient .....	91	20	2.73	0.6	0.125

In the equilibrium  $2K^+ + 2HSO_3' \rightleftharpoons 2KHSO_3 \rightleftharpoons K_2S_2O_5 + H_2O$ , if *x* be the initial concentration of potassium hydrogen sulphite and *y* that of the metabisulphite, we have, the concentration of water being constant,  $x^2/y = K$ . Neglecting ionisation and taking *y* as small compared with *x*, then, if the concentration be halved, the concentration of potassium hydrogen sulphite will be *x*/2 and the new concentration, *y'*, of potassium metabisulphite will be given by  $(x^2/4)/y' = K$ , whence  $y' = y/4$ . This agrees with the observed facts, a discrepancy being caused by ionisation, which increases with dilution and hence reduces the effective concentration of the potassium hydrogen sulphite. It may therefore be concluded that the absorption band at  $257 \mu\mu$ , initially shown by solutions of potassium metabisulphite and solutions of sulphur dioxide half neutralised by sodium, potassium, or rubidium hydroxide, is due to a small proportion of metabisulphite present in the equilibrium. It is evident that the concentration of the metabisulphite is small from a comparison of the molecular extinctions of solutions of potassium metabisulphite and of  $SO_2, xH_2O$  of equal molecular concentration. Thus, with 0.025*M*-solutions, the molecular extinction of the metabisulphite is 5, whilst that of  $SO_2, xH_2O$  is 171. In a solution, therefore, of a bisulphite of this concentration there is present metabisulphite to the extent of 2.9 per cent. of the amount of  $SO_2, xH_2O$  present in a solution of sulphur dioxide of the same concentration, the  $SO_2, xH_2O$  being itself only a proportion of the total sulphur dioxide content.

The following series of equilibria therefore exist in an air-free solution of potassium metabisulphite or potassium hydrogen sulphite:

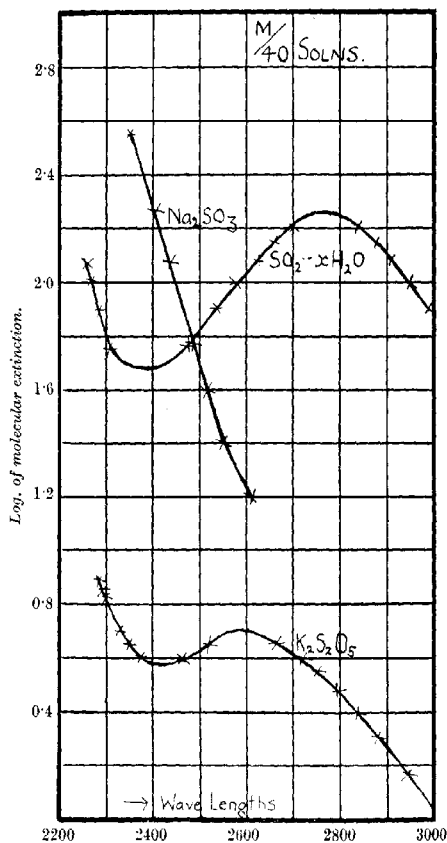


with the result that the solution shows the absorption band due to



dioxide is 135.1, and therefore the wave-numbers of the three bands should be integral multiples of this. The following table shows that this relationship holds good, the shift of about  $1.8\ \mu\mu$  towards

FIG. 3.



the red being the normal effect observed with solutions as compared with gases.

	Wave-number of band.	Wave-length of band calc.	Wave-length of band obs.	Origin of band.
$25 \times 135.1$	3377.5	$296.1\ \mu\mu$	$296.1\ \mu\mu$	$\text{SO}_2$
$27 \times 135.1$	3647.7	$274.1\ \mu\mu$	$276.0\ \mu\mu$	$\text{SO}_2.x\text{H}_2\text{O}$
$20 \times 135.1$	3917.9	$255.2\ \mu\mu$	$257.0\ \mu\mu$	$\text{K}_2\text{SO}_5.\text{SO}_2$

*Summary.*

(1) In aqueous solutions of bisulphites there is present in the equilibrium a small proportion of metabisulphite which absorbs light of wave-length  $257\ \mu\mu$ .

(2) In the absence of oxygen, these solutions are stable in light, but if oxygen is present photo-oxidation of the  $\text{HSO}_3$  ion takes place, followed by an ionic rearrangement whereby normal sulphate, sulphurous acid, and hydrated sulphur dioxide are produced. The solution then shows the absorption band at  $\lambda = 276\ \mu\mu$  characteristic of the hydrated sulphur dioxide.

(3) No isomerism of sulphite molecules has been detected. The absorption bands of sulphurous acid, bisulphite, and sulphite molecules lie in the extreme ultra-violet.

(4) The characteristic ultra-violet frequencies of sulphur dioxide, hydrated sulphur dioxide, and potassium metabisulphite are integral multiples of the fundamental molecular frequency of sulphur dioxide in the infra-red.

In conclusion, we tender our thanks to the Department of Scientific and Industrial Research for a grant to one of us (R. A. B.) which has enabled this investigation to be carried out.

THE UNIVERSITY,  
LIVERPOOL.

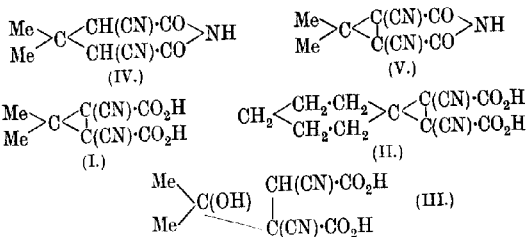
[Received, July 22nd, 1922.]

CCXX.—*The Formation and Stability of spiro-Compounds. Part IX. The Influence on Stability of Groups of High Molecular Weight.*

By STANLEY FRANCIS BIRCH and JOCELYN FIELD THORPE.

IN Part VI of this series (F., 1921, 119, 1315) it was shown that the relative stability of the cyclohexane derivative (II) as compared with that of the dimethyl compound (I), due to the alteration of the tetrahedral angle of  $109.5^\circ$  in the latter case to  $107.2^\circ$  in the former, was of such an order as to render it possible to detect the effect of the change by means of a reaction, carried out under mild conditions, which was then described.

It was found, for example, that the dicyano-acid (I) readily underwent ring fission, yielding the hydroxy-acid (III), whereas the cyclohexane acid (II), under similar conditions, remained unchanged.



This method seemed, therefore, likely to be a useful one for determining the comparative stability of similarly constituted ring structures, and this proved to be the case, for it has now been found that the reaction by which the dicyanodicarboxylic acids (types I and II) were prepared is a general one and that these compounds, or their fission products, can always be prepared from the relevant imide (type V) under special conditions.

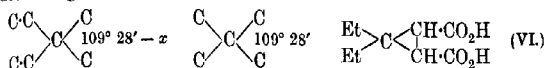
In brief, the method involves the preparation of the Guareschi compound (IV) (in this case from acetone), its conversion into the ring imide (V) by the aid of bromine, and the hydrolysis of this to the dicyanodicarboxylic acid (II) when it is stable, or to the hydroxy-open-chain acid (III) when ring fission occurs.

It is evident that by employing a selected number of the many ketones which yield Guareschi compounds, a large field is at once opened for the study of ring structures, differing only in the character of the groups attached to the  $\beta$ -carbon atom, and which are therefore admirably suited for purposes of comparison.

The discovery of the new method is of importance for two reasons. In the first place, it is more sensitive than that hitherto used, which involved a study of the relative stability of the *cyclopropane* acids of the general type (VI), a comparison which is strictly limited in its application because, excepting in the case of the derivative in the *gem*-dimethyl series which yields terebic acid, it was not found possible to isolate any definite products owing to the fact that ring fission was accompanied in every case by deep-seated degradation, leading to the formation of much free carbon. Secondly, it provided a means whereby it would be possible to investigate the behaviour of groups of molecular weight greater than that of the methyl group on the stability of the ring systems under discussion.

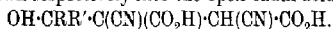
It will be remembered that although we have, in the earlier parts of the series, established our hypothesis regarding the effect of angle change, caused by a definite alteration of the tetrahedral angle, due to the inclusion of two of the valencies of the  $\beta$ -carbon atom in a ring complex, experiments have recently been carried out (com-

pare Deshapande and Thorpe, this vol., p. 1430) which show that the effect, on the next carbon atom of a chain, of two linked carbon atoms is greater than that of one.



Thus the behaviour of the diethyl compound (VI), as regards its stability and also as shown by the occurrence of tautomerism between its hydroxy-derivative and the open-chain form, indicated that the *gem*-diethyl group exercised an effect on the tetrahedral angle which was between that caused by the dimethyl group and that produced by the cyclohexane ring.

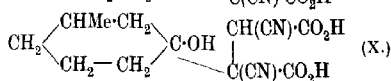
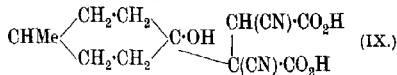
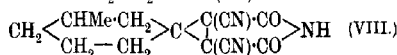
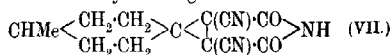
We have therefore examined the stability of the dicyanodicarboxylic acids,  $\text{CRR}'\text{C}(\text{CN})\text{CO}_2\text{H}$ , from diethyl ketone,  $\text{R} = \text{R}' = \text{Et}$ , from methyl *n*-hexyl ketone,  $\text{R} = \text{Me}$ ;  $\text{R}' = \text{C}_6\text{H}_{13}$ , from cyclopentanone,  $\text{R} + \text{R}' = \text{C}_4\text{H}_8$ , and from benzyl methyl ketone,  $\text{R} = \text{Me}$ ;  $\text{R}' = \text{CH}_2\text{Ph}$ , and we find that all these substances are broken down respectively into the open-chain acids,



It is evident, therefore, that none of these ring acids approaches in stability that derived from cyclohexanone (II) and that the attachment of groups of high molecular weight and those having long carbon chains does not affect the tetrahedral angle to an extent greater than that exercised by the cyclohexane complex. The method, unfortunately, does not enable us to differentiate between those compounds which undergo fission because, under the experimental conditions employed, the ring is either completely destroyed or it remains unattacked. In other words, the reaction is so rapid that it does not appear to be possible to devise any series of experiments by which its rate might be determined. It is hoped, however, that another method of attack, which is now being investigated, will give us the desired information.

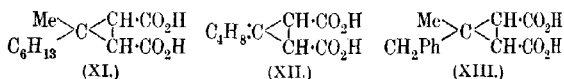
It is desirable to place on record two curious facts which have been discovered during the course of this investigation, but for which we are not, at present, in a position to offer an adequate explanation. Having established, from our experiments in the dimethyl and diethyl series and those described in this paper, the fact that the volume of a carbon atom attached to one of the valencies of a carbon atom is increased by the linking of another carbon atom to it, but that this volume effect is small, even when six carbon atoms are linked as in the methyl hexyl series, compared with that produced by the cyclohexane ring, we decided to ascertain whether any change in the tetrahedral angle could be detected

by replacing one of the hydrogen atoms of the *cyclohexane* ring by a methyl group. We prepared, therefore, the ring imides (VII) and (VIII) from 4- and 3-methyl*cyclohexanone*, respectively, and found that the presence of the methyl group had in each case destroyed the stability characteristic of the unsubstituted ring dicyano-acid (II) and that the hydroxy-acids (IX) and (X) were the sole products formed by the reagent used.

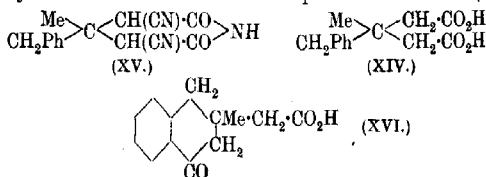


More experimental work on this important point is needed before we can draw a definite conclusion as to the cause of this remarkable change in stability.

It was mentioned in Part VI (*loc. cit.*) that the degradation of the cyclic imides (type V) constituted a useful method for preparing *cyclopropane* derivatives of type VI. The experiments in the present communication still further illustrate this point, and the acids (VI), (XI), (XII), and (XIII) have been prepared by this means:



Indeed, in the case of the benzyl methyl acid (XIII), the process is, apparently, the only obvious one by which the cyclic acid can be obtained, because, as shown by Kon and Stevenson (T., 1921, 119, 87), the glutaric acid (XIV) from which it would otherwise have to be prepared cannot be obtained by the hydrolysis of the Guareschi compound (XV), since the conditions necessary to produce hydrolysis lead to the formation of the naphthalene derivative (XVI)



It is important to note that all these acids were prepared through the amide of type  $\text{CRR}'\text{C}(\text{CH}\cdot\text{CN})\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ , which is readily produced from the ring imide of type V by a method described in the experimental portion.

#### EXPERIMENTAL.

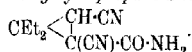
The dicyano-imides required for this research were prepared by the modification of Guareschi's method described by Kon (T., 1921, 119, 818; compare also Kon and Thorpe, T., 1919, 115, 693) and were used for the next preparation without further purification.

##### *Derivatives of Diethylcyclopropane.*

*The Imide of 2:3-Dicyano-1:1-diethylcyclopropane-2:3-dicarboxylic Acid*,  $\text{CEt}_2\text{C}(\text{CN})\text{C}(\text{CN})\text{CO}\cdot\text{NH}_2$ .—The preparation of this compound has been described by Guareschi, but it is more conveniently obtained by a similar method to that used in preparing the dimethyl derivative in Part VI (*loc. cit.*).

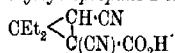
The dicyano-imide (0.1 gram-mol.) was suspended in 100 c.c. of 80–90 per cent. formic acid, and 4 c.c. of the bromine were added with vigorous shaking; the solid dissolved and the solution became warm. Water was then added until the dibromo-compound commenced to separate, and was followed by the rest of the bromine (6 c.c.). The mixture was boiled for twenty minutes and allowed to cool, when the bridged imide separated; it was collected, washed with water, and dried. The yield was usually 60 per cent. of that theoretically possible, but a further small quantity separated on diluting the mother-liquor with water. The imide thus obtained melted at 202–204° and was used without further purification.

*2:3-Dicyano-1:1-diethylcyclopropane-2-carboxylamide*,



—This amide was prepared from the above imide in the same way as the corresponding dimethyl derivative; it separated as an oil, which readily solidified on cooling. The yield was quantitative. The amide crystallises from benzene in small, colourless prisms melting at 123–124° (Found: N = 22.03.  $\text{C}_{10}\text{H}_{13}\text{ON}_3$  requires N = 21.98 per cent.).

*2:3-Dicyano-1:1-diethylcyclopropane-2-carboxylic Acid*,



—This acid was obtained in 80 per cent. yield by the action of nitrous acid on the amide, using the same conditions as those



described for the preparation of the dimethyl acid. No unchanged amide was recovered. The acid crystallises from dilute hydrochloric acid in fine needles melting at  $148^{\circ}$  (Found: N = 14.49.  $C_{10}H_{13}O_2N_2$  requires N = 14.57 per cent.).

*The Dinitrile of 1:1-Diethylcyclopropane-2:3-dicarboxylic Acid,*  
 $CEt_2 \begin{array}{c} \text{CH}\cdot\text{CN} \\ | \\ \text{CH}\cdot\text{CN} \end{array}$ —On heating the above acid with a little water in

a sealed tube at  $180^{\circ}$ , the nitrile separated as an oil, which, after the usual purification (dimethyl derivative, Part VI, *loc. cit.*), distilled at  $184^{\circ}/22$  mm. The yield is 70 per cent.; nothing could be isolated from the alkaline washings.

When pure, the dinitrile is a light yellow, odourless oil which shows no tendency to solidify (Found: N = 18.92.  $C_8H_{11}N_2$  requires N = 18.91 per cent.).

*cis- and trans-1:1-Diethylcyclopropane-2:3-dicarboxylic Acid (VI).*—A mixture of the two forms of this acid was obtained in theoretical yield, by hydrolysing the dinitrile in the same way as the dimethyl derivative. The two forms were isolated by the method described by Deschamps and Thorpe (*loc. cit.*).

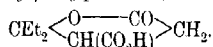
The *trans*-acid, which formed more than 90 per cent. of the mixed acids, possessed all the properties described and was shown to be identical by direct comparison (mixed melting point). It crystallised from water in small, colourless prisms, melting at  $241^{\circ}$  (Found: C = 57.91; H = 7.62. Calc., C = 58.04; H = 7.58 per cent.). Titration with 0.01924N-barium hydroxide (Found: 30 c.c. Calc., 29.8 c.c.).

Only a small quantity of the *cis*-acid appeared to be formed and this was not isolated in a pure condition (melting point  $155\text{--}160^{\circ}$ ).

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -ethylpentane- $\alpha\alpha\beta$ -tricarboxylic Acid,*  
 $CEt_2 \begin{array}{c} \text{O} \text{---} \text{CO} \\ | \quad \diagup \\ \text{CH}(\text{CO}_2\text{H}) \end{array} \text{CH}\cdot\text{CO}_2\text{H}$ .—This substance was obtained by hydrolysing the amide with excess of aqueous potassium hydroxide solution; the yield was theoretical.

The lactone crystallises from water or dilute hydrochloric acid in elongated prisms, melting and decomposing at  $172^{\circ}$  (Found: C = 51.86; H = 6.13.  $C_{10}H_{11}O_6$  requires C = 52.16; H = 6.11 per cent.).

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -ethylpentane- $\alpha\beta$ -dicarboxylic Acid,*



—This acid was obtained by boiling the above lactone with excess of 50 per cent. sulphuric acid for three hours. On standing, the new acid separated in large, colourless octahedra which, after crystallisation from water, melted at  $105^{\circ}$ . The quantity obtained

was insufficient for analysis, but gave two end-points on titration with 0.01924*N*-barium hydroxide, corresponding with one free carboxyl group and one lactone ring (Found : 10.05 e.c., 20.4 e.c. Calc., 10 e.c., 19.9 e.c.).

*αβ-Dicyano-γ-hydroxy-γ-ethylpentane-αβ-dicarboxylic Acid*,  
 $\text{OH}\cdot\text{C}(\text{CN})_2\cdot\text{C}(\text{CN})(\text{CO}_2\text{H})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$ .

—This acid is formed when the imide is boiled with 10 per cent. potassium hydroxide solution for half an hour and separates in glistening prisms on acidifying the cold solution. The new acid forms small, glistening prisms from water and melts with vigorous decomposition at 194–195° (Found : C = 52.25; H = 5.65.  $\text{C}_{11}\text{H}_{14}\text{O}_5\text{N}_2$  requires C = 51.96; H = 5.55 per cent.).

#### *Derivatives of Methyl-n-hexylcyclopropane.*

*Preparation of the Imide of 2:3-Dicyano-1-methyl-1-n-hexylcyclopropane-2:3-dicarboxylic Acid*,  $\text{C}_6\text{H}_{13}\cdot\text{CMe}\begin{smallmatrix} \text{C}(\text{CN})\cdot\text{CO} \\ \text{C}(\text{CN})\cdot\text{CO} \end{smallmatrix}\text{NH}$ .—This

imide was prepared by the original method described by Guareschi (*Mem. R. Accad. Sci. Torino*, 1901, **50**, 235), the dibromo-derivative being isolated and heated for several days on the water-bath with a large excess of 50 per cent. acetic acid. Finally, this was allowed to evaporate and the residue crystallised from alcohol. The imide, so obtained, is very impure and contains a considerable quantity of the unbridged imide, formed by the partial hydrolysis of the dibromo-derivative under the conditions employed. It can be obtained pure only after many recrystallisations from dilute acetic acid.

*2:3-Dicyano-1-methyl-1-n-hexylcyclopropane-2-carboxylamide*,  $\text{C}_6\text{H}_{13}\cdot\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CN} \\ \text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2 \end{smallmatrix}$ .—This amide separates as an oil on boiling a solution of the crude imide in slightly more than one molecular proportion of 10 per cent. potassium hydroxide solution. On cooling, it solidifies and is collected; the mother-liquor yields a second crop on further heating. The *amide* crystallises from benzene or methyl alcohol in colourless needles melting at 119° (Found : N = 18.33.  $\text{C}_{12}\text{H}_{16}\text{ON}_3$  requires N = 18.01 per cent.).

The formation of this amide proved to be of great use, as it provided a simple means of isolating the bridged derivatives in a pure condition. For this reason, the crude imide was not purified, but was converted into the amide, in which form it could be readily purified.

*2:3-Dicyano-1-methyl-1-n-hexylcyclopropane-2-carboxylic Acid*,  $\text{C}_6\text{H}_{13}\cdot\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CN} \\ \text{C}(\text{CN})\cdot\text{CO}_2\text{H} \end{smallmatrix}$ .—This acid is formed when the amide

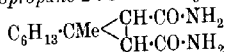
is treated with nitrous acid in the usual way. It remains, on removal of the ether, as a colourless oil, which, although it tends to solidify, cannot be further purified. The yield of the crude acid is good (Found: N = 11.76.  $C_{13}H_{18}O_2N_2$  requires N = 11.96 per cent.).

The silver salt, prepared in the usual way, could not be obtained colourless, but had a slight yellow colour (Found: N = 8.72; Ag = 31.97.  $C_{13}H_{17}O_2N_2Ag$  requires N = 8.21; Ag = 31.66 per cent.).

*The Dinitrile of 1-Methyl-1-n-hexyleycyclopropane-2:3-dicarboxylic Acid*,  $C_6H_{13} \cdot CMe \begin{smallmatrix} \text{CH} \cdot \text{CN} \\ \text{CH} \cdot \text{CN} \end{smallmatrix}$ .—On heating the above acid at  $180^\circ$  with a little water in a sealed tube, the nitrile is formed in 60—70 per cent. yield and floats on the water. After the usual purification, it distils at  $205^\circ/17$  mm. The nitrile thus obtained is a colourless liquid with a characteristic odour (Found: N = 14.59.  $C_{12}H_{16}N_2$  requires N = 14.73 per cent.).

*Hydrolysis of the Dinitrile*.—The nitrile was hydrolysed in the usual way by boiling with a large excess of aqueous potassium hydroxide, alcohol being added to give a homogeneous solution. After a short time, a distinct odour resembling that of methyl hexyl ketone became noticeable, and as it was feared that the trimethylene ring was undergoing fission, the hydrolysis was stopped. These fears, however, proved to be groundless, the odour being traced to the nitrile, but as a result of the incomplete hydrolysis, several nitrogenous products were found to be present.

On cooling the alkaline solution, a small quantity of solid separated; it was collected and after being crystallised from dilute alcohol, melted at  $277^\circ$ . Analysis proved it to be the diamide of trans-1-methyl-1-n-hexyleycyclopropane-2:3-dicarboxylic acid,



(Found: N = 12.45.  $C_{12}H_{22}O_2N_2$  requires N = 12.49 per cent.).

The filtrate from the diamide was extracted with ether to remove any other neutral substances, but other than a little nitrile, nothing was recovered. The solution was then strongly acidified, the oil which separated extracted with ether, the ether evaporated, and the semi-solid residue dissolved in hot alcohol with the addition of animal charcoal. The filtered solution deposited a quantity of a colourless acid on cooling; this was collected and after recrystallisation from the same solvent, melted at  $206\text{--}207^\circ$ . An analysis showed it to be the monoamide of trans-1-methyl-1-n-hexyleycyclopropane-2:3-dicarboxylic acid,  $C_6H_{13} \cdot CMe \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$  (Found:

C = 63.45; H = 9.47; N = 6.24.  $C_{12}H_{21}O_3N$  requires C = 63.38; H = 9.33; N = 6.21 per cent.). Titration with 0.01924 *N*-barium hydroxide (Found: 24.7 c.c. Calc., 25.2 c.c.).

The proof of the constitution of this acid was obtained by hydrolysing it further with aqueous potassium hydroxide. In this way a non-nitrogenous acid was obtained which was exceedingly difficult to purify and was analysed as the *silver* salt for this reason. It was undoubtedly *trans*-1-methyl-1-n-hexylcyclopropane-2:3-dicarboxylic acid (Found: C = 32.51; H = 4.11.  $C_{12}H_{19}O_4Ag$  requires C = 32.58; H = 4.13 per cent.).

The alcoholic mother-liquor, from which this amide had separated, was evaporated to dryness, and the gum obtained examined for the presence of the *cis*-acid by heating it for some time with a large excess of acetyl chloride. A small amount of solid was formed, which was filtered off, and the excess of reagent removed in a vacuum. The remaining gum was distilled, and boiled at 180°/13 mm.; the oil obtained was identified as the *anhydride* of *cis*-1-methyl-1-n-hexylcyclopropane-2:3-dicarboxylic acid,  $C_6H_{13} \cdot CMe \begin{smallmatrix} \diagup CH \cdot CO \\ \diagdown CH \cdot CO \end{smallmatrix} > O$ , by its general behaviour and by analysis (Found: C = 68.30; H = 8.74.  $C_{12}H_{16}O_3$  requires C = 68.54; H = 8.61 per cent.).

The *anhydride* is a colourless oil which shows no tendency to solidify; it is slowly decomposed by water, but dissolves readily in dilute aqueous potassium hydroxide solution with the formation of the potassium salt of the *cis*-acid. The latter is obtained on acidifying this solution and crystallises from benzene in a mass of felted needles, melting with slight decomposition at 106–107° (Found: C = 62.96; H = 8.72.  $C_{12}H_{20}O_4$  requires C = 63.11; H = 8.85 per cent.).

The *anilic acid*,  $C_6H_{13} \cdot CMe \begin{smallmatrix} \diagup CH \cdot CO \cdot NHPh \\ \diagdown CH \cdot CO_2H \end{smallmatrix}$ , prepared in the usual way, crystallises from alcohol in colourless plates, melting and decomposing at 137.5° (Found: C = 71.66; H = 8.33.  $C_{18}H_{25}O_3N$  requires C = 71.28; H = 8.20 per cent.).

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -methylnonane-2 $\alpha$ :3-tricarboxylic Acid*,  $C_6H_{13} \cdot CMe \begin{smallmatrix} \diagup O \\ \diagdown CH(CO_2H) \end{smallmatrix} \text{---} CO > CH \cdot CO_2H$ .—When the amide was hydrolysed by an excess of aqueous potassium hydroxide and the acidified solution extracted with ether, the new lactone remained as a gum on evaporating the ethereal extract. It showed no tendency to solidify and was not analysed.

The constitution follows from its conversion into the lactone to be described below, which takes place to some extent on boiling in aqueous solution, and from its method of formation.

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -methylnonane- $\alpha\beta$ -dicarboxylic Acid,*  
 $C_6H_{13} \cdot CMe \left\langle \begin{array}{c} O \text{---} CO \\ CH(CO_2H) \end{array} \right\rangle CH_2$ .—This acid separates in theoretical yield on boiling the above gum with dilute sulphuric acid (15 per cent.) for two hours. The oily acid obtained crystallises from dilute methyl alcohol in plates and melts at  $183^\circ$  (Found: C = 63.26; H = 8.82.  $C_{12}H_{20}O_4$  requires C = 63.11; H = 8.85 per cent.). Titration with 0.0192N-barium hydroxide (Found: 28.7 c.c. Calc., 28.5 c.c.).

*$\alpha\beta$ -Dicyano- $\gamma$ -hydroxy- $\gamma$ -methylnonane- $\alpha\beta$ -dicarboxylic Acid,*  
 $C_6H_{13} \cdot CMe(OH) \cdot C(CN)(CO_2H) \cdot CH(CN) \cdot CO_2H$ .—This acid was obtained by boiling a solution of the imide in 10 per cent. aqueous potassium hydroxide (3 mols.) for half an hour, and acidifying the cold solution with hydrochloric acid. The plastic solid which separated, crystallised from dilute hydrochloric acid in colourless plates melting and decomposing at  $183^\circ$  (Found: C = 56.98; H = 6.93.  $C_{11}H_{20}O_5N_2$  requires C = 56.73; H = 6.81 per cent.).

#### Derivatives of Benzylmethyleyclopropane.

*Preparation of the Imide of 2:3-Dicyano-1-benzyl-1-methyleyclopropane-2:3-dicarboxylic Acid,*  $\begin{array}{c} Me \\ \diagup \\ CH_2Ph \end{array} > C \left\langle \begin{array}{c} C(CN) \cdot CO \\ C(CN) \cdot CO \end{array} \right\rangle NH$ .—The method was a modification of that described by Guareschi (*Gazzetta*, 1918, 48, ii, 83).

The finely powdered imide (0.1 gram-mol.) was suspended in 160 c.c. of 50 per cent. acetic acid in a separating funnel, and 10 c.c. of bromine were added slowly with vigorous shaking. The dibromoderivative thus obtained was washed into a large beaker by means of 100 c.c. of 50 per cent. formic acid and boiled for fifteen minutes. Water was then added to precipitate the bridged imide as far as possible, and the crystalline precipitate collected, washed with water, and dried. The yield is quantitative. The imide crystallises from dilute alcohol in small, colourless needles melting at  $261\text{--}262^\circ$ .

*2:3-Dicyano-1-benzyl-1-methyleyclopropane-2-carboxamide,*  
 $\begin{array}{c} Me \\ \diagup \\ CH_2Ph \end{array} > C \left\langle \begin{array}{c} CH \cdot CN \\ C(CN) \cdot CO \cdot NH_2 \end{array} \right\rangle$ .—This amide separates as an oil in theoretical yield on boiling a solution of the imide (1 mol.) in 10 per cent. aqueous potassium hydroxide (1 mol.) for a few minutes.

On cooling, it solidifies, and can be crystallised from dilute alcohol or benzene, from which it forms short needles melting at  $123.5^\circ$  (Found: N = 17.71.  $C_{11}H_{13}ON_3$  requires N = 17.57 per cent.).

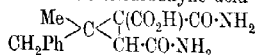
*2:3-Dicyano-1-benzyl-1-methyleyclopropane-2-carboxylic Acid,*  
 $\begin{array}{c} Me \\ \diagup \\ CH_2Ph \end{array} > C \left\langle \begin{array}{c} CH \cdot CN \\ C(CN) \cdot CO_2H \end{array} \right\rangle$ .—Considerable difficulty was encountered

in the preparation of this acid. When the amide was treated with nitrous acid in the usual way, nothing other than highly coloured gums could be isolated from the reaction mixture.

Owing to the tendency for the benzylmethyl derivatives to pass into naphthalene derivatives with acid hydrolysing agents, it was necessary to find a method of preparing the acid without the use of acids. This was ultimately accomplished by the use of the alternative method described for the preparation of the corresponding dimethyl acid, that is, the direct hydrolysis of the imide by two molecular proportions of 10 per cent. aqueous potassium hydroxide.

Twenty-six grams of the imide were dissolved in 56 c.c. of 10 per cent. potassium hydroxide, an equal volume of methyl alcohol was added, and the mixture boiled for an hour under reflux. At the end of this time the condenser was removed and the alcohol allowed to evaporate. The cooled solution was then extracted twice with ether to remove any amide formed by partial hydrolysis of the imide, and after being strongly acidified, extracted repeatedly with ether. During this operation a considerable quantity of solid separated, and this was collected; the wet ether solution also deposited a further quantity, the total amounting to 6 grams.

This substance on examination proved to be an acid, sparingly soluble in all the usual organic solvents and consequently very difficult to purify. It was identified as the 2 : 3-diamide of 1-benzyl-1-methylcyclopropane-2 : 2 : 3-tricarboxylic acid



(Found : C = 61.10; H = 6.15.  $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_2$  requires C = 60.83; H = 5.83 per cent.).

The acid crystallises from ethyl acetate in small prisms melting and decomposing at 197°.

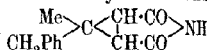
On removing the ether from the ethereal extract, a gum remained, which, after much rubbing with light petroleum, solidified. All attempts to purify this substance further failed; on slow crystallisation from ethyl acetate, some more of the acid described above was obtained, but the residue remained as a gum. It was found, however, that it contained a considerable amount of the required acid and therefore it was used for the preparation of the nitrile; the rest probably consists of the acid, melting at 197°, which gives rise to the imide formed during this preparation.

The Dinitrile of 1-Benzyl-1-methylcyclopropane-2 : 3-dicarboxylic Acid,  $\begin{array}{c} \text{Me} \\ \text{CH}_2\text{Ph} \end{array} > \text{C} < \begin{array}{l} \text{CH}\cdot\text{CN} \\ \text{CH}\cdot\text{CN} \end{array}$ .—When the crude acid described above was heated with water in a sealed tube at 180°, it was found that no oil separated until the tube was cold. The contents of

several tubes were united, acidified, and repeatedly extracted with ether; the ethereal extract was carefully washed, first with sodium hydrogen carbonate solution, then with dilute potassium hydroxide, and finally with water. After drying over calcium chloride, the ether was evaporated and the oil obtained left in an exhausted desiccator over-night. On the next day a considerable amount of crystalline matter was found to have separated and this was collected. It was identified as the *trans*-1-benzyl-1-methylcyclopropane-2:3-dinitrile (Found: N = 14.60.  $C_{13}H_{12}N_2$  requires N = 14.28 per cent.). It crystallises from dilute methyl alcohol in large, transparent plates melting at  $91^\circ$ ; on hydrolysis with potassium hydroxide, it gives a theoretical yield of the *trans*-1-benzyl-1-methylcyclopropane-2:3-dicarboxylic acid (see below).

The mother-liquor, from which this nitrile had separated, was distilled, and boiled from  $210$ — $220^\circ/13$  mm.; on standing, the distillate deposited a considerable quantity of the above compound, but although the *cis*-form of the nitrile could not be isolated, proof of its presence was found in the products of alkaline hydrolysis.

On acidification, the potassium hydroxide washings gave an oil which solidified on keeping and after crystallisation from dilute alcohol melted at  $102$ — $103^\circ$ ; from this solvent, it forms small clusters of needles. It was proved, by its hydrolysis to the *cis*-form of 1-benzyl-1-methylcyclopropane-2:3-dicarboxylic acid and by analysis, to be the imide of this acid,



(Found: C = 72.66; H = 6.12.  $C_{13}H_{13}O_2N$  requires C = 72.60; H = 6.00 per cent.).

The separation of the acids obtained from the sodium bicarbonate washings was not attempted owing to the complex nature of the mixture.

*trans*-1-Benzyl-1-methylcyclopropane-2:3-dicarboxylic Acid (XIII).—This acid, as has been stated above, is obtained in theoretical yield by the hydrolysis of the nitrile, melting at  $91^\circ$ , by potassium hydroxide.

The acid crystallises from dilute alcohol in characteristic clusters of small, stout needles, melting at  $210^\circ$  (Found: C = 66.56; H = 6.04.  $C_{13}H_{14}O_4$  requires C = 66.63; H = 6.02 per cent.). Titration with 0.01924N-barium hydroxide (Found: 23.5 c.c.; Calc., 23.1 c.c.).

The *anilide*,  $\text{CH}_2\text{Ph} \begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_2\text{Ph} \end{array} \begin{array}{c} \text{CH}\cdot\text{CO}\cdot\text{NHPh} \\ | \\ \text{CH}\cdot\text{CO}\cdot\text{NHPh} \end{array}$ , obtained by treating the acid chloride (from the acid and thionyl chloride) with aniline in benzene solution, separates from alcohol in an indefinite, flocculent mass, melting at  $245^\circ$  (Found: C = 78.25; H = 6.38.  $C_{25}H_{25}O_2N_2$  requires C = 78.09; H = 6.30 per cent.).

*cis*-1-Benzyl-1-methylcyclopropane-2:3-dicarboxylic Acid (XIII).

—This acid was obtained by hydrolysing the imide melting at 102–103° with potassium hydroxide solution. On crystallisation from dilute alcohol, it forms flattened needles melting at 179–180° and decomposing at 185° (Found: C = 66.84; H = 6.15.  $C_{13}H_{14}O_4$  requires C = 66.63; H = 6.02 per cent.).

The *anhydride*,  $\text{Me} > \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CO} \\ \text{CH} \cdot \text{CO} \end{smallmatrix} > \text{O}$ , was obtained by heating the acid with excess of acetyl chloride for an hour, evaporating off the excess in a vacuum, and crystallising the residual solid from a mixture of benzene and light petroleum (b. p. 40–60°). It forms characteristic clusters of prisms melting at 105° (Found: C = 72.26; H = 5.56.  $C_{13}H_{12}O_3$  requires C = 72.19; H = 5.60 per cent.).

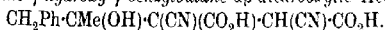
The *anilic acid*,  $\text{Me} > \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{NHPh} \\ \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , prepared from the anhydride in the usual way, crystallises from alcohol in colourless plates melting at 152° (Found: C = 73.90; H = 6.26.  $C_{19}H_{16}O_3N$  requires C = 73.68; H = 6.21 per cent.).

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -benzylbutane- $\alpha\alpha\beta$ -tricarboxylic Acid*,  $\text{Me} > \text{C} \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} > \text{CH} \cdot \text{CO}_2\text{H}$ .—This lactone is obtained in quantitative yield when the amide is hydrolysed with potassium hydroxide (compare dimethyl compound). It crystallises from water in fine, colourless plates melting and decomposing at 173° (Found: C = 60.63; H = 5.06.  $C_{14}H_{14}O_6$  requires C = 60.42; H = 5.07 per cent.).

*Lactone of  $\gamma$ -Hydroxy- $\gamma$ -benzylbutane- $\alpha\beta$ -dicarboxylic Acid*,  $\text{Me} > \text{C} \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} > \text{CH}_2$ .—On boiling the above lactone with dilute sulphuric acid (10 per cent.), a mixture of two acids is obtained, which can be separated by means of hot benzene.

The soluble acid crystallises in prisms and melts, rather indefinitely, at 140°; it was shown by analysis to be the above lactone (Found: C = 66.81; H = 6.31.  $C_{13}H_{14}O_4$  requires C = 66.63; H = 6.02 per cent.).

The insoluble acid resisted all attempts at purification; it is probable that it is a naphthalene derivative, but, as it did not form a semicarbazone, no evidence could be obtained to support this view.

 *$\alpha\beta$ -Dicyno- $\gamma$ -hydroxy- $\gamma$ -benzylbutane- $\alpha\beta$ -dicarboxylic Acid*,

—The imide was dissolved in 10 per cent. aqueous potassium hydroxide solution (3 mols.) and boiled for half an hour. It was



then cooled and acidified, when a quantity of a plastic solid separated. As this contained potassium, it was boiled with water, the insoluble residue collected, and an equal volume of hydrochloric acid added to the hot solution. On cooling, the new acid crystallised in colourless plates, free from potassium; a further amount was recovered from the insoluble residue, which proved to be the free acid in a crude condition, by crystallisation from dilute alcohol. The acid crystallises from dilute alcohol in small plates, melting and decomposing vigorously at  $203^{\circ}$  (Found: C = 59.62; H = 4.64; N = 9.39.  $C_{15}H_{14}O_5N_2$  requires C = 59.61; H = 4.66; N = 9.27 per cent.).

*Derivatives of cycloPentanespirocyclopropane.*

*The Imide of cycloPentanespiro-2 : 3-dicyanocyclopropane-2 : 3-dicarboxylic Acid*,  $C_4H_8 \cdot C \begin{smallmatrix} \diagup C(CN) \cdot CO \\ \diagdown C(CN) \cdot CO \end{smallmatrix} > NH$ .—This imide is obtained in quantitative yield by the method described for the preparation of the diethyl compound (p. 1825). It crystallises from alcohol in fine, colourless needles which lose their crystalline form on drying and melt at  $195$ — $196^{\circ}$  (Found: C = 60.83; H = 4.23; N = 19.66.  $C_{11}H_8O_2N_3$  requires C = 60.47; H = 4.34; N = 19.53 per cent.).

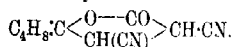
*cycloPentanespiro-2 : 3-dicyanocyclopropane-2-carboxylamide*,  $C_4H_8 \cdot C \begin{smallmatrix} \diagup CH \cdot CN \\ \diagdown C(CN) \cdot CO \cdot NH_2 \end{smallmatrix} >$ .—On hydrolysing the imide with potassium hydroxide (1 mol.) in the manner described for the preparation of these amides, the new amide separates in 75—80 per cent. of the theoretical yield. A further quantity can be recovered by heating the mother-liquor again. The *amide* crystallises from alcohol or benzene in fine, colourless needles melting at  $150^{\circ}$  (Found: C = 63.45; H = 5.69.  $C_{10}H_{11}ON_3$  requires C = 63.46; H = 5.87 per cent.).

*cycloPentanespiro-2 : 3-dicyanocyclopropane-2-carboxylic Acid*,  $C_4H_8 \cdot C \begin{smallmatrix} \diagup CH \cdot CN \\ \diagdown C(CN) \cdot CO_2H \end{smallmatrix} >$ .—This acid was obtained in 80 per cent. yield by the action of nitrous acid on the above amide, using the method described for the preparation of the dimethyl compound. It crystallises from water in prisms, melting without decomposing at  $169$ — $170^{\circ}$  (Found: C = 63.46; H = 5.31.  $C_{10}H_{10}O_2N_2$  requires C = 63.13; H = 5.31 per cent.).

*The Dinitrile of cycloPentanespirocyclopropane-2 : 3-dicarboxylic Acid*,  $C_4H_8 \cdot C \begin{smallmatrix} \diagup CH \cdot CN \\ \diagdown CH \cdot CN \end{smallmatrix} >$ .—On heating the above acid with a little water in a sealed tube at  $180^{\circ}$ , the nitrile separates as an oil which, after extraction with ether and the usual purification, distils at

186°/13 mm. The nitrile thus obtained is a colourless oil which solidifies on keeping and crystallises from a mixture of ether and light petroleum (b. p. under 40°) in long, colourless needles melting at 43° (Found: N = 19.14.  $C_5H_{10}N_2$  requires N = 19.16 per cent.).

Although nothing could be isolated from the alkaline washings, a small quantity of what was undoubtedly a fission product was obtained by evaporating the original aqueous layer. Although the amount obtained was too small for analysis, it was shown that, on further hydrolysis with alkalis, this substance is converted into the lactic acid described below. It therefore appears likely that the acid is represented by the formula



*cis- and trans-cycloPentanespirocyclopropane-2 : 3-dicarboxylic Acid (XII).*—When the nitrile was hydrolysed by potassium hydroxide in the manner described for the hydrolysis of the dimethyl derivative, a theoretical yield of the mixed *spiro*-acids was obtained.

The acids were separated by crystallisation from water, the *trans*-form being the less soluble and forming nearly 90 per cent. of the total mixed acids.

The *trans*-acid crystallised from water in characteristic clusters of short, stout needles, melting at 210°, and possessed all the properties of the *spiro*-acid described by Becker and Thorpe (T., 1920, 117, 1579), who give the melting point as 211° (Found: C = 58.54; H = 6.65. Calc., C = 58.70; H = 6.57 per cent.). Titration with 0.01924N-barium hydroxide (Found: 29.5 c.c. Calc., 29.5 c.c.).

The presence of a small quantity of the *cis*-acid in the mother-liquor was shown by evaporating to dryness and boiling the residue with acetyl chloride for a short time. Under these conditions, the *trans*-acid remains insoluble and can be removed; the *cis*-acid, which remains in solution as the anhydride, can then be isolated in the usual way or as its anilic acid.

In this way, a small amount of the anilic acid, corresponding with, roughly, 5 per cent. of the total mixed acids, was isolated. It crystallised from alcohol in colourless prisms melting at 191–192° (Becker and Thorpe, *loc. cit.*, give 187°).

*Lactone of 1-Hydroxycyclopentylethane-2,2,3-tricarboxylic Acid,*  $C_4H_8 \cdot C \begin{array}{c} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}(\text{CO}_2\text{H}) \end{array} > \text{CH} \cdot \text{CO}_2\text{H}$ .—This lactone was obtained by boiling the amide with excess of potassium hydroxide solution until ammonia ceased to be evolved, acidifying, and extracting with ether. The required lactone remained as a gum on evaporating the ether, and readily solidified on rubbing with a glass rod. It

crystallises from dilute hydrochloric acid or water in small prisms melting at  $159^{\circ}$  (Found: C = 52.71; H = 5.18.  $C_{10}H_{12}O_6$  requires C = 52.61; H = 5.30 per cent.).

*Lactone of 1-Hydroxycyclopentylethane- $\alpha\beta$ -dicarboxylic Acid,*  
 $C_4H_8 \cdot C \begin{array}{c} \diagup O \diagdown \\ \diagdown CH(CO_2H) \diagup \end{array} CO \rangle CH_2$ .—The new acid is obtained in quantitative yield by boiling the above lactone with 20 per cent. sulphuric acid for two hours. It separates as an oil which readily solidifies on keeping. It crystallises from water in nacreous plates melting at  $134^{\circ}$  (Found: C = 58.57; H = 6.65.  $C_9H_{10}O_4$  requires C = 58.70; H = 6.57 per cent.).

*$\alpha\beta$ -Dicyano-1-hydroxycyclopentylethane- $\alpha\beta$ -dicarboxylic Acid,*  
 $C_4H_8 \cdot C(OH) \cdot C(CN)(CO_2H) \cdot CH(CN) \cdot CO_2H$ .

—This acid was obtained in 70 per cent. yield by boiling a solution of the imide in 10 per cent. aqueous potassium hydroxide (3 mols.) for half an hour. The acid separates on acidifying the cold solution. It crystallises from water in rhombic plates melting with vigorous decomposition at  $188^{\circ}$  (Found: C = 52.49; H = 4.93.  $C_{11}H_{10}O_3N_2$  requires C = 52.40; H = 4.76 per cent.).

*Derivatives of 3- and 4-Methylcyclohexanespirocyclohexane.*

The preparation of the bridged imides has been described by Squintani (*Atti R. Accad. Sci. Torino*, 1912—1913, **48**, 685), but they are more conveniently prepared by the method used to prepare the cyclohexane derivative (Part VI, *loc. cit.*).

*$\alpha\beta$ -Dicyano-1-hydroxy-3-methylcyclohexylethane- $\alpha\beta$ -dicarboxylic Acid (X).*—The imide was dissolved in 10 per cent. aqueous potassium hydroxide (3 mols.) and the solution boiled for half an hour. It was then cooled and acidified with hydrochloric acid; on standing, the new acid separated, contaminated with the potassium salt. It was therefore dissolved in as little boiling water as possible and an equal volume of hydrochloric acid added to the hot solution. On cooling, the pure acid separated; it was crystallised from dilute alcohol. The acid forms colourless prisms melting with vigorous decomposition at  $212^{\circ}$  (Found: C = 56.08; H = 5.89.  $C_{13}H_{14}O_3N_2$  requires C = 55.68; H = 5.71 per cent.).

*$\alpha\beta$ -Dicyano-1-hydroxy-4-methylcyclohexylethane- $\alpha\beta$ -dicarboxylic Acid (IX).*—This acid, prepared in exactly the same way as the acid just described, separates almost completely as the potassium salt. After dissolving in water and adding concentrated hydrochloric acid, the acid was obtained as a colourless mass. It crystallised from water in small prisms melting with vigorous decomposition at  $207^{\circ}$  (Found: C = 55.98; H = 5.67.  $C_{13}H_{14}O_3N_2$  requires C = 55.68; H = 5.67 per cent.).

We are indebted to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the cost of this research.

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### CCXXI.—*The Solubilities of the Alkali Formates and Acetates in Water.*

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THE object of this work was to determine the influence of the alkali metal in these salts on their solubility, and on the formation of hydrates, and to compare it with that observed with the salts of inorganic acids.

For several of the salts solubility measurements have already been published: lithium, sodium, and potassium formates (Groschuff, *Ber.*, 1903, **46**, 1790); sodium acetate (Green, *J. Physical Chem.*, 1908, **12**, 1655); potassium acetate (Abe, *J. Tokio Chem. Soc.*, 1911, **32**, 980). Very few measurements seem to have been made of the ice curves except those of Rüdorff (*Ann. Physik*, 1922, **145**, 616) on sodium acetate, which appear to be affected by some systematic error, as his values of the depression are in all cases much smaller than ours.

We have extended and completed these observations; we have determined the ice curves for all the ten salts, and the salt (solubility) curves for the five of them (rubidium and caesium formates, lithium, rubidium, and caesium acetates) which had not previously been examined.

*Preparation of Materials.*—The formic acid was obtained from the commercial 80 per cent. acid by distillation in a vacuum at 70° with enough sulphuric acid to form with the water present the monohydrate (Maquenne, *Bull. Soc. chim.*, 1888, [ii], **50**, 622). The product melted at 6°. The acetic acid was three times boiled with potassium permanganate and distilled, the middle portion alone being collected (Bousfield and Lowry, *T.*, 1911, **99**, 1432). The lithium salts were prepared by precipitating lithium sulphate solution with the barium salt of the organic acid, the others by neutralising the carbonate or hydroxide with the acid.

The rubidium carbonate was made from a specimen of the alum very kindly given to us by Mr. K. M. Chance, of the British Cyanides Company, to whom our best thanks are due. The alum contained a few units per cent. of both potassium and caesium. The

former was removed by six recrystallisations from water, after which the product was spectroscopically free from potassium. To remove the cesium, the alum was treated with excess of pure barium hydroxide, the sulphate filtered off, and the filtrate, after saturating with carbon dioxide and again filtering, evaporated to dryness. A repetition of this process renders the alumina insoluble, and the alkaline carbonates can be extracted with water. The barium precipitates must be repeatedly boiled with water to remove adherent salts. The mixed rubidium and cesium carbonates were then converted into the acid tartrates, which were recrystallised from water (Allen, *Amer. J. Sci.*, 1862, [ii], 34, 367). After four recrystallisations, the salt gave no indication of cesium in the spectroscope. The acid tartrates repress one another's solubility to a remarkable degree: the rubidium salt is almost insoluble in a saturated solution of the cesium salt. We are greatly indebted to Major W. C. Ball for suggestions as to the purification of the rubidium salt, and to Professor T. R. Merton for kindly carrying out the spectroscopic tests. The rubidium hydrogen tartrate was finally converted into the carbonate by ignition.

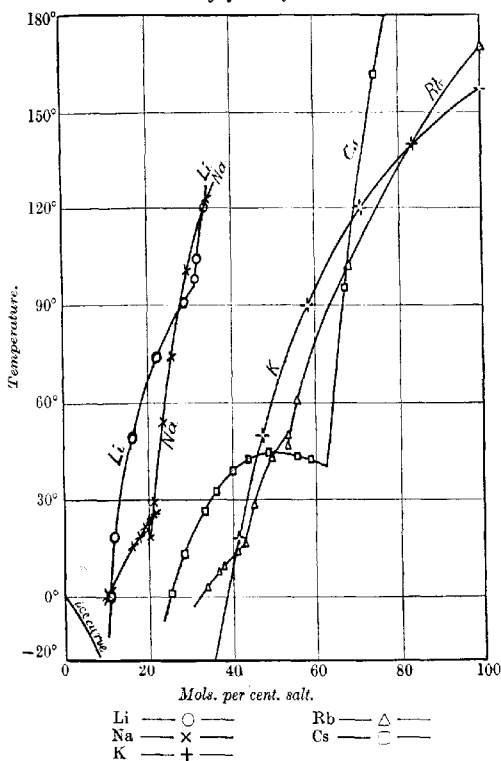
The cesium was obtained from a specimen of American pollucite, being separated as the double antimony chloride, and then converted into the nitrate, and thence through the oxalate into the carbonate. Both the rubidium and the cesium carbonates obstinately retained traces of colloidal carbon, which could be removed only by repeated evaporation and ignition.

*Measurement of Solubility and Ice Curves.*—The freezing points were measured in a Beckmann apparatus. The determinations at higher temperatures were usually made synthetically by sealing up weighed quantities of the components in tubes, and observing the temperature at which the last crystals disappeared on slow warming. In some cases the solution was filtered, and analysed by evaporation to dryness. The solutions of the acetates (but not those of the formates) showed a strong tendency to supersaturation.

*Examination of the Solid Phases.*—At the highest temperatures examined (150° and above) it could be assumed that the solid phase was the anhydrous salt, and the formation of a hydrate could be inferred from a break in the curve. In some cases the hydrate curves gave maxima, the positions of which indicated the composition. Otherwise the hydrate was, if possible, obtained in crystals large enough to be cleaned and analysed. The residue method was not applicable on account of the great solubility, the high viscosity of the solutions, and often the small size of the crystals which were formed. Solutions of rubidium acetate con-

taining a slight excess of acetic acid very readily deposited crystals of an acid salt; but these were not formed in the entire absence of free acid. This acetate, when anhydrous, has a strong tendency (not shared by any other acetate examined) to absorb the vapour of acetic acid.

FIG. 1.  
*Solubility of alkali formates.*



The following solid phases were observed by ourselves or by earlier workers (A = formate or acetate radicle):—

*Formates.*—Lithium: Groschuff (*loc. cit.*) found LiA and LiA, H<sub>2</sub>O.

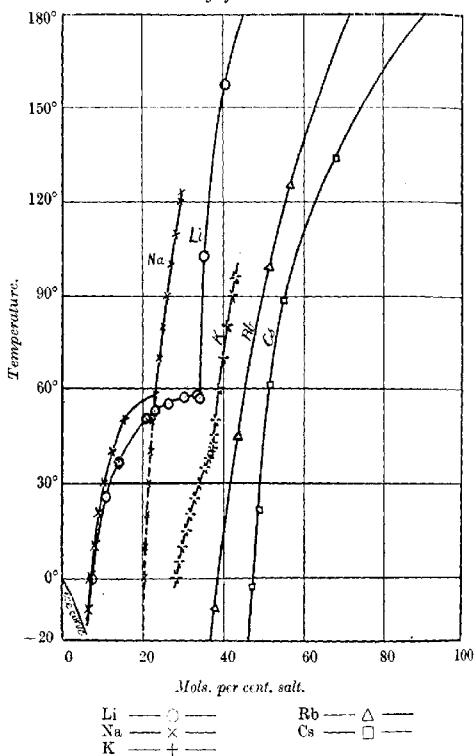
These results were confirmed. The anhydrous salt melts with slight decomposition at 279–280° (corr.).

(Sodium: NaA, 3H<sub>2</sub>O, NaA, 2H<sub>2</sub>O, and NaA, the last melting at 253° [Groschuff]).

(Potassium: KA, m. p.  $157^{\circ}$ ; no hydrates [Groschuff]).

Rubidium: RbA, small leaflets, m. p.  $170^{\circ}$  (corr.). At  $51^{\circ}$  (in contact with the solution) this changes to a hydrate ( $<1\text{H}_2\text{O}$ ,  $? \frac{1}{2}\text{H}_2\text{O}$ ), small, tetragonal prisms, and this at  $16.5^{\circ}$  goes into a higher hydrate (small prisms,  $?1\text{H}_2\text{O}$ ). If formic acid is heated

FIG. 2.  
*Solubility of alkali acetates.*



at about  $105^{\circ}$  in contact with the anhydrous salt, it decomposes with separation of carbon, although the salt alone is quite stable at this temperature. This is presumably due to a secondary decomposition of the carbon monoxide into dioxide and carbon.

Cæsium: CsA, prisms, m. p.  $265^{\circ}$  (corr.) without decomposition. CsA,  $\text{H}_2\text{O}$  (from position of maximum on curve: the crystals were

too small for analysis). Tetragonal prisms, m. p. (congruent)  $45^{\circ}$ . Transition point  $41^{\circ}$ .

*Acetates*.—Lithium: LiA, m. p.  $286^{\circ}$  (corr.) with very slight decomposition. At  $56.5^{\circ}$  this changes into LiA,  $2H_2O$  (found, by direct analysis,  $2.04H_2O$ ), rhombic, with congruent melting point at  $57.8^{\circ}$ . This dihydrate is already described by Schabus (*Jahresber.*, 1854, 433). No evidence was obtained of the monohydrate mentioned by Rammelsberg (*Ann. Physik*, 1820, 66, 82).

(Sodium: This is stated by Green [*loc. cit.*] to give a hydrate, NaA,  $3H_2O$ , which passes at  $58^{\circ}$  into NaA, melting at  $323^{\circ}$  [uncorr.]. We found the melting point to be  $330^{\circ}$  [corr.].)

(Potassium: Abe [*loc. cit.*] describes a hydrate, KA,  $1\frac{1}{2}H_2O$ , changing at  $41^{\circ}$  into KA,  $\frac{1}{2}H_2O$ , which at about  $96^{\circ}$  goes into KA; m. p.  $292^{\circ}$ ).

Rubidium: RbA, leaflets, as described by Grandeau (*Ann. Chim. Phys.*, 1863, [iii], 67, 234), m. p.  $246^{\circ}$  (corr.). An acid salt, crystallising in needles, is formed on addition of a small excess of acetic acid.

Cæsium: CsA, m. p.  $194^{\circ}$  (corr.) without decomposition.

TABLE I.

*Formates.*

Lithium.				Rubidium (continued).			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
5.80	2.088	— $4.27^{\circ}$	ice	85.60	45.05	$28.3^{\circ}$	$\frac{1}{2}$ aq.
10.98	4.095	— $9.02$	"	87.77	49.75	$43.6$	"
17.86	7.002	— $16.42$	"	89.23	53.34	$49.9$	"
				89.23	53.34	$46.9^*$	0
Sodium.				—	—	$51.0$	$\frac{1}{2}+0$
7.24	2.024	— $4.29$	ice	90.06	55.55	$60.8$	0
11.42	3.301	— $7.02$	"	93.89	67.95	$101.7$	0
16.95	5.127	— $11.02$	"	(m. p.)	100	$170$	0
24.86	8.035	— $18.04$	"				
Potassium.				4.00	0.420	— $0.77$	ice
5.71	1.280	— $2.62$	ice	8.11	0.886	— $1.72$	"
12.95	3.086	— $6.72$	"	14.29	1.662	— $3.44$	"
18.42	4.611	— $10.42$	"	19.62	2.414	— $5.27$	"
25.03	6.678	— $15.82$	"	26.75	3.476	— $8.12$	"
26.04	7.246	— $17.39$	"	77.07	25.37	+ $1.0$	1 aq.
Rubidium.				81.69	31.09	$21.0$	"
6.23	0.909	— $1.82$	ice	83.25	33.44	$26.2$	"
15.93	2.549	— $5.62$	"	84.81	36.09	$32.2$	"
20.62	3.463	— $7.82$	"	86.88	40.11	$39.2$	"
25.79	4.573	— $10.62$	"	88.67	44.18	$42.7$	"
30.62	5.744	— $13.88$	"	90.42	48.83	$44.6$	"
78.86	33.97	+ $3.3$	1 aq.	(m. p.)	50	$45.0$	"
80.71	36.59	$7.8$	"	92.54	55.61	$43.8$	"
81.37	37.59	$9.5$	"	93.47	59.14	$42.6$	"
83.59	41.09	$14.0$	"	—	—	$41$	$1+0$
84.61	43.12	$16.3$	"	95.27	67.07	$95.4$	0
—	—	$16.5$	$1+\frac{1}{2}$ aq.	96.67	75.49	$161.6$	"
				(m. p.)	100	$265$	"

\* Metastable point.



TABLE II.

*Acetates.*

Lithium.				Potassium.			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
2.63	0.732	- 1.54°	ice	5.00	0.957	- 2.15°	ice
4.83	1.367	- 2.98	"	7.42	1.450	- 3.36	"
9.52	2.794	- 6.62	"	17.04	3.631	- 9.32	"
18.33	5.777	-16.12	"	20.53	4.630	-12.32	"
23.76	7.830	± 0	2 aq.	25.50	5.914	-17.92	"
31.28	11.04	+25.8	"	Rubidium.			
38.25	14.45	36.7	"	9.59	1.306	- 2.79	ice
49.55	21.13	50.5	"	16.11	2.339	- 5.27	"
52.23	22.97	53.3	"	19.64	2.957	- 6.82	"
56.60	26.24	55.4	"	25.57	4.100	-10.27	"
61.92	30.72	57.3	"	82.92	37.68	- 9.50	0
(m. p.)	33.33	57.8	"	86.23	43.82	+44.7	"
64.25	33.65	57.8	"	89.30	50.97	99.4	"
64.88	34.35	57.0	0	91.35	56.82	125.2	"
66.73	35.04	102.8	"	(m. p.)	100	246	"
71.33	40.43	157.5	"	Cæsium.			
(m. p.)	100	286	"	6.63	0.662	- 1.36	ice
				19.38	2.207	- 5.32	"
				25.26	3.077	- 7.92	"
				34.22	4.659	-13.07	"
				89.71	47.00	- 2.5	0
				91.06	48.74	+21.5	"
6.107	1.407	- 2.96	ice	91.98	51.82	61.1	"
11.27	2.712	- 6.42	"	93.09	55.81	88.6	"
16.62	4.192	-11.12	"	95.78	68.03	133.8	"
20.57	5.378	-15.17	"	(m. p.)	100	194	"

All these salts, when anhydrous, are very deliquescent. In each case a small quantity was heated in a tube for several hours to a temperature a little below its melting point, and then the tube was sealed while still hot and the melting point determined.

The results are collected in the preceding tables, the first column giving the percentage by weight, the second the molecular percentage, the third the temperature, and the fourth the solid phase in contact with the solution (0 = anhydrous salt). They are plotted (using molecular percentages) on Figs. 1 and 2, the salt curves of lithium, sodium, and potassium formates being taken from the results of Groschuff, that of sodium acetate from Green, and that of potassium acetate from Abe (*loc. cit.*).

*Discussion of Results.*

In comparing the solubilities of the salts of the different alkali metals, it is necessary to consider the molecular percentages (which are given in the diagrams), and to confine the comparison to the anhydrous salt curves; all that can be said of the hydrates is

that they must be less soluble than the anhydrous salts at the same temperature. The accepted rule is that with the salts of weak acids the solubility increases with the atomic weight of the alkali metal, but that with strong acids the reverse is the case. Our results show that the formates and acetates on the whole follow this rule, as the salts of weak acids.

The following are the solubilities in molecular percentages at  $100^{\circ}$ , as obtained by interpolation from the curves. The value for potassium acetate refers to the hydrate,  $\text{KA}_2\text{H}_2\text{O}$ , but as the transition point, according to Abc, is very near  $100^{\circ}$ , the solubility of the anhydrous salt should not be very different. All the other values refer to the anhydrous salts.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cesium.
Formate .....	31.7	29.8	62.1	67.4	67.7
Acetate .....	34.9	27.2	43.0	51.2	58.3

The only marked exception is in the relative positions of the lithium and sodium salts. In the formates, the lithium salt is the more soluble below  $120^{\circ}$ , and in the acetates it is so throughout. In both series the lithium and sodium salts are markedly less soluble than those of the other metals. In comparing any property of the alkali metals as a group, it will often be found (as, for example, with the ionic velocities) that they tend to fall into two sub-groups, the distinction between sodium and potassium being much more marked than that between any other two consecutive members.

The formation of hydrates by rubidium and caesium formates is very surprising, especially as no hydrate of the potassium salt was detected by Groschuff. The tendency to form hydrates certainly diminishes as a rule as the atomic weight of the alkali metal increases, and it is generally believed that rubidium seldom, and caesium never, forms hydrated salts, with the exception of double salts such as the alums. Our results show that this is not true of the organic salts, and further examples are given in the following paper.

One of us (J. A. H. R. G.) is in receipt of a Salters' Fellowship, for which he wishes to express his gratitude.

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CCXXII.—*The Solubility of the Alkali Salts of Benzoic and the Hydroxybenzoic Acids in Water.*

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In a previous paper (T., 1921, **119**, 979), we have shown that there is a great difference in volatility and solubility between *o*-hydroxybenzoic acid and its *m*- and *p*-isomerides. The object of the work described in the present paper was to determine whether this difference extended to the salts of these acids, and also to throw further light on the effect of the alkali metal on their solubilities and on their power of forming hydrates.

The published data as to the solubilities of these salts scarcely extend beyond a few measurements at the ordinary temperature of some of the benzoates and salicylates (Hoitsema, *Z. physikal. Chem.*, 1898, **27**, 315, sodium salicylate at 20°: Greenish and Smith, *Pharm. J.*, 1901, **65**, 774, 806, the same at 15°: Pajetta, *Gazzetta*, 1906, **36**, II, 67, potassium benzoate at 17—50°: Seidell, *J. Amer. Chem. Soc.*, 1909, **31**, 1164 and *U.S. Dept. of Public Health*, 1910, Bull. **67**, 91, lithium and sodium benzoates and salicylates at 25°: Pellini, *Atti R. Acad. Lincei*, 1910, **19**, I, 331, sodium benzoate at 25° and 40°). Previous descriptions of the salts themselves will be referred to later.

*Preparation of Materials.*—The lithium salts were made by precipitating lithium sulphate solution with the barium salt of the acid; the sodium and other salts by neutralising the acid with the corresponding hydroxide or carbonate. The rubidium carbonate had been prepared in this laboratory by Mr. J. A. H. R. Gentle, by the method described in the preceding paper, from a specimen of the alum for which we are indebted to the kindness of Mr. K. M. Chance. The caesium salt was made from a specimen of American pollucite. The rubidium and caesium salts were tested spectroscopically, and found to be free from other alkali metals.

*Determination of Solubility.*—In a few instances this was done analytically, by evaporating to dryness a weighed quantity of the saturated solution. At higher temperatures, the solutions were usually too viscous to allow of this, and the measurements were made synthetically, by enclosing weighed quantities of the salt and water in small tubes, and observing the temperatures at which the last crystals disappeared on slow warming.

*Examination of the Solid Phases.*—The measurements could not be carried up to the melting points of the anhydrous salts, owing to their decomposition; but they were extended to temperatures at which it was obvious that the solid phase must be anhydrous.

Where a break in the curve indicated the formation of a solid hydrate, its composition was determined by direct analysis if it could be obtained in sufficiently large crystals. If this was impossible, the "residue" method was adopted. A small quantity of the chloride of the alkali metal was added to the saturated solution, and after filtering off any organic salt that might be precipitated (and might enclose solid chloride) the liquid was stirred for some time with excess of the solid hydrate; the latter was then filtered off, and the amount of chloride in the filtrate and in the moist solid determined by Volhard's method. The amount of water in each phase was estimated by drying at  $100^{\circ}$ , and in this way the quantity of water in the dry hydrate could be calculated. The results are not very accurate; the great solubility of the solid salt makes the liquid very viscous, so that the separation of the two phases is very imperfect, and it also depresses the solubility of the chloride to a few units per cent., which diminishes the accuracy of the titration. But the results are good enough to decide between different formulæ for the hydrate. With rubidium *o*-hydroxybenzoate and rubidium and cesium *m*-hydroxybenzoates, the small size of the crystals and the high solubility and viscosity of the solutions made the use of this method impossible.

The following solid phases were observed (A = acid radicle):—

*Benzoates*.—Lithium:  $\text{LiA}, \text{H}_2\text{O}$ . Analysed directly (found 1.09 mol. of water to 1 mol. of salt).  $\text{LiA}$ , stable above  $34^{\circ}$ .\*

Sodium and potassium: both anhydrous. Sestini (*Bull. Soc. chim.*, 1870, [ii], **13**, 488) describes the preparation (by evaporation of the aqueous solution) of two salts,  $\text{NaA}, \text{H}_2\text{O}$  and  $\text{KA}, 3\text{H}_2\text{O}$ , which he analysed by driving off the water by heat. He does not state how he freed them from the very viscous mother-liquor. The solubility curves give no indication of the formation of either of these hydrates. With potassium, the formation of an acid salt was observed, but it was not further examined. Gerhardt (*Jahresber.*, 1852, 450) obtained an acid benzoate,  $\text{KA}, \text{HA}$ , by the action of benzoic anhydride on potassium acetate in alcohol; he describes it as only slightly soluble in cold water.

Rubidium: Anhydrous. Crystallises well, in large, flat prisms. An acid salt separates in small quantity from the neutral solution; its formation during the solubility measurements was prevented by adding a slight excess of carbonate.

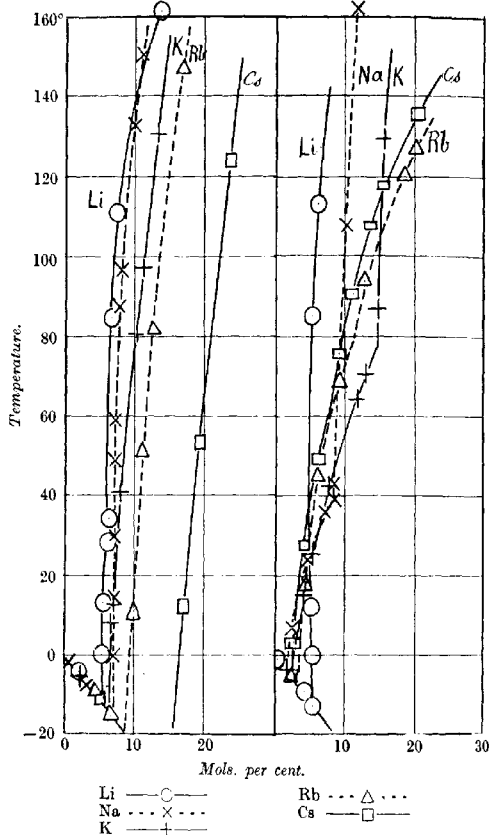
Cesium: Anhydrous; apparently isomorphous with the rubidium salt.

*o*-Hydroxybenzoates.—Lithium: (1)  $\text{LiA}, 6\text{H}_2\text{O}$ ; this salt could

\* The transition temperatures were taken from the curves.

not be analysed, but the solubility curve is tending to a maximum near 14.3 mols. per cent., so that we can assume that like the sodium salt it contains six molecules of water. It changes at  $-1^{\circ}$

FIG. 1. Solubility of benzoates. FIG. 4. Solubility of p-hydroxybenzoates.



into (2)  $\text{LiA} \cdot \text{H}_2\text{O}$  (found, by direct analysis, 0.83 mol. of water).  
(3)  $\text{LiA}$ , stable above  $53^{\circ}$ .

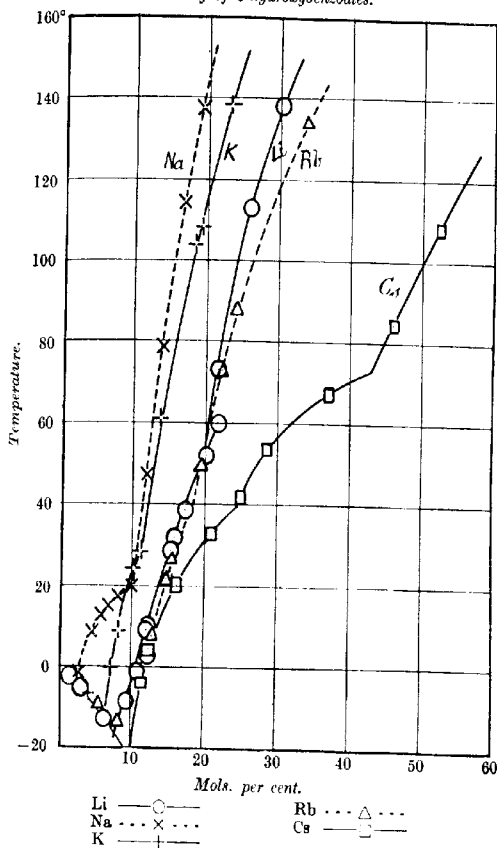
Sodium:  $\text{NaA} \cdot 6\text{H}_2\text{O}$  (found, by direct analysis, 6.06 mols.  $\text{H}_2\text{O}$ ). Massol (*Ann. Chim.*, 1894, [vii], 1, 217) states that the

commercial salt contains  $1\text{H}_2\text{O}$ , but we found no such salt. The hexahydrate goes over into the anhydrous salt at  $20^\circ$ .

Potassium:  $\text{KA}\cdot\text{H}_2\text{O}$  (found, by residue method, 1.02 mols.  $\text{H}_2\text{O}$ ); goes into the anhydrous salt at  $29^\circ$ .

FIG. 2.

*Solubility of o-hydroxybenzoates.*

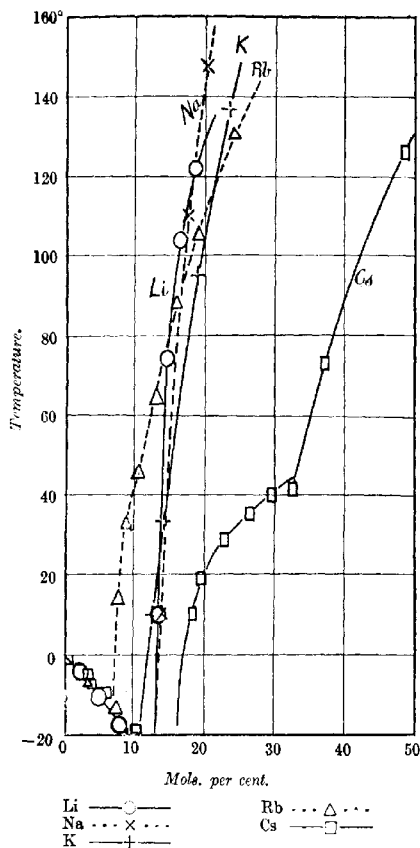


Rubidium: Probably monohydrate (found, by dehydration of air-dried crystals, 0.76 mol.  $\text{H}_2\text{O}$ ). Its crystalline properties were altered by heating to  $100^\circ$ ; goes into the anhydrous salt at  $40^\circ$ .

Cesium: (1)  $\text{CsA}\cdot\text{H}_2\text{O}$  (found 1.15 mols.  $\text{H}_2\text{O}$  by dehydration

at 100°). (2)  $\text{CsA} \cdot \frac{1}{2}\text{H}_2\text{O}$  (?), a lower hydrate which could not be analysed, and which is stable between 39° and 74°. (3)  $\text{CsA}$ .

FIG. 3.  
Solubility of *m*-hydroxybenzoates.



Hoffmann (*Jahresber.*, 1877, 759) prepared acid salts of the *o*-hydroxybenzoates of lithium, sodium, and potassium.

*m*-Hydroxybenzoates.—The lithium, sodium, and potassium salts are all anhydrous.

Rubidium:  $\text{RbA}, \text{H}_2\text{O}$  (found, by residue method, 1.14 mols.  $\text{H}_2\text{O}$ ); stable up to  $47^\circ$ .

Cæsium:  $\text{CsA}, x\text{H}_2\text{O}$ . Owing to the fineness of the crystals and the high concentration of the solution this salt could not be analysed; but its occurrence is clear from the break in the solubility curve at  $45^\circ$ . This could not be due to an acid salt, since its position was not altered by the addition of 4 per cent. of cæsium carbonate to the solution.

*p-Hydroxybenzoates*.—Lithium: anhydrous.

Sodium:  $\text{NaA}, 5\text{H}_2\text{O}$  (found, by dehydration at  $100^\circ$ , 5.03 mols.  $\text{H}_2\text{O}$ ); described by Hartmann (*J. pr. Chem.*, 1877, [ii], 16, 35); goes into the anhydrous salt at  $39^\circ$ .

Potassium:  $\text{KA}, 3\text{H}_2\text{O}$  (found, by dehydration, 3.12 mols.  $\text{H}_2\text{O}$ ); described by Hartmann (*loc. cit.*); goes into the anhydrous salt at  $79^\circ$ .

TABLE I.

## Benzoates.

Lithium.				Potassium.			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
7.22	1.082	-1.69°	Ice	5.04	0.594	-0.86°	Ice
13.69	2.181	-3.94		9.70	1.193	-2.14	
19.85	3.365	-6.49	1 aq.	16.23	2.131	-4.29	"
27.97	5.179	± 0		24.23	3.471	-7.31	
29.80	5.633	+13.5	"	39.89	6.950	+8.5	0
32.12	6.239	28.5		40.60	7.140	13.0	
33.20	6.532	34.5	"	44.92	8.410	41.0	"
34.61	6.928	84.5		0	50.99	10.49	
36.51	7.482	111.0	"	53.50	11.46	97.5	"
45.14	10.37	162.4		58.42	13.65	131.0	
49.12	11.97	176.0	"	66.09	17.99	181.0	"

Sodium.				Rubidium.				
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.	
8.36	1.127	-2.02	Ice	9.41	0.897	-1.56	Ice	
16.52	2.414	-4.85		21.15	2.285	-4.71		
26.01	4.210	-8.50	0	33.32	4.181	-9.04	"	
38.52	7.265	± 0		45.75	6.844	-14.75		
38.59	7.284	+15.0	"	56.06	10.02	+15.0	0	
38.60	7.288	30.0		59.70	11.45	51.5		
38.70	7.316	49.2	"	63.23	13.05	82.0	"	
39.20	7.460	59.7		70.32	17.13	147.0		
41.26	8.070	87.6	"	Cæsium.				
42.28	8.388	97.0						
47.30	10.09	133.0	"	9.92	0.774	-1.22	Ice	
50.75	11.41	151.3		25.62	2.380	-4.44		
57.05	14.24	186.0	"	43.08	5.091	-10.81	"	
60.43	16.03	204.5		74.75	17.34	+12.0		
				77.34	19.47	53.5	"	
				81.51	23.80	124.0		



Rubidium:  $\text{RbA} \cdot \text{H}_2\text{O}$  (found, by dehydration, 1.04 mols.  $\text{H}_2\text{O}$ ); goes into  $\text{RbA}$  at  $78^\circ$ .

Cæsium:  $\text{CsA} \cdot \text{H}_2\text{O}$  (found, by dehydration, 1.08 mols.  $\text{H}_2\text{O}$ ); stable up to  $64^\circ$ .

The results of the solubility measurements are contained in Tables I—IV, and are plotted (using molecular concentrations) in Figs. 1—4.

TABLE II.  
*o*-Hydroxybenzoates.

Lithium.				Potassium.			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
10.17	1.396	-2.26*	Ice	10.49	1.185	-1.82*	Ice
20.62	3.145	-5.56	"	18.82	2.316	-3.47	"
35.83	6.525	-12.82	"	31.15	4.422	-6.52	"
45.25	9.365	-8.5	6 aq.	35.80	5.394	-8.00	"
49.04	10.74	-1.0	"	44.08	7.464	$\pm 0$	1 aq.
52.45	12.12	+9.0	1 aq.	49.19	8.450	+9.0	"
52.96	12.34	+3.5*	6 aq.	53.33	10.46	24.0	"
"	"	10.0	1 aq.	55.82	11.45	28.5	"
56.50	15.41	28.5	"	61.31	13.95	61.0	0
57.50	15.98	32.0	"	68.97	18.53	103.8	"
59.67	17.22	38.5	"	70.20	19.42	108.5	"
64.18	20.13	52.0*	"	74.80	23.29	138.2	"
66.56	21.87	60.0*	"	Rubidium.			
"	"	73.0	0	12.34	1.127	-1.62	Ice
71.46	26.04	113.0	"	23.48	2.424	-3.69	"
75.77	30.32	138.0	"	33.81	3.968	-6.34	"
Sodium.				42.77	5.706	-8.82	"
4.94	0.581	-0.77	Ice	53.40	8.488	-13.17	"
13.15	1.675	-2.65	"	64.85	12.99	+8.0	1 aq.
21.18	2.935	-5.04*	"	68.15	14.77	21.5	"
20.06	2.746	-1.5	6 aq.	69.84	15.79	27.0	"
29.61	4.519	+9.0	"	74.97	19.53	49.0	0
35.03	5.718	12.5	"	77.96	22.26	73.0	"
40.48	7.107	15.2	"	79.89	24.34	88.0	"
44.40	8.242	17.5	"	86.36	33.88	134.0	"
50.00	10.11	20.0	"	Cæsium.			
55.10	12.08	47.5	0	16.08	1.264	-1.83	Ice
59.32	14.09	78.5	"	30.97	2.907	-4.24	"
64.16	16.77	114.0	"	47.71	5.740	-8.08	"
67.95	19.27	137.0	"	65.70	11.32	-3.5	1 aq.
				68.24	12.53	+4.5	"
				74.59	16.37	20.5	"
				80.07	21.13	33.0	"
				83.35	25.03	41.5*	$\frac{1}{2}$ aq.
				85.67	28.50	54.0	"
				89.91	37.28	67.5	"
				92.80	46.00	84.3	0
				94.33	52.58	107.5	"

\* Metastable point.

TABLE III.  
*m*-Hydroxybenzoates.

Lithium.				Rubidium.			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
16.02	2.33	-4.41°	Ice	14.92	1.399	-2.23°	Ice
29.58	4.99	-10.78	"	32.13	3.690	-6.41	"
39.97	7.68	-17.67	"	48.88	7.184	-13.69	Ice +
52.53	13.46	+10.0	0				1 aq.
55.04	14.68	74.5	"	50.61	7.658	+14.0	1 aq.
58.47	16.52	104.0	"	54.94	8.982	32.5	"
61.86	18.57	122.0	"	60.02	10.83	45.0	"
				65.04	13.10	64.0	0
				70.45	16.17	88.0	"
				74.49	19.11	105.0	"
				79.91	24.35	130.0	"
Sodium.				Cesium.			
14.68	1.899	-3.21	Ice	16.98	1.348	-1.97	Ice
30.53	4.71	-8.85	"	32.84	3.160	-4.92	"
45.16	8.48	-17.52	"	48.53	5.919	-9.65	"
58.78	13.82	+10.0	0	63.15	10.25	-18.50	"
64.61	17.94	110.0	"	77.10	18.34	+10.0	x aq.
69.75	20.60	147.5	"	78.52	19.61	19.0	"
				81.70	22.95	29.0	"
				84.45	26.60	35.0	"
				86.35	29.67	40.0	"
				87.88	32.60	41.5*	0
				89.88	37.21	73.0	"
				93.42	48.64	126.5	"

\* Metastable point.

*Discussion of Results.*

The results clearly show that the anomalous differences found in the solubilities of the free hydroxybenzoic acids do not extend to their salts, among which no marked differences are to be observed. It is therefore evident that these anomalies depend on some chemical change in which the hydrogen of the carboxyl group takes part, since they vanish when this hydrogen is replaced by a metal.

The general conclusion which emerges as to the influence of the alkali metal is that (as we should expect with the salts of weak acids) the solubility of the anhydrous salt increases with the atomic weight of the metal. This is true over the greater part of the range with only one exception, lithium *o*-hydroxybenzoate, which is more soluble than the sodium and potassium salts: this may be due to the salt not being isomorphous with its isomerides. The interpolated values in molecular percentages of the solubilities of the salts at 100° (where they are all anhydrous) are as follow:

Metal.	Li.	Na.	K.	Rb.	Cs.
Benzoate .....	7.24	8.48	11.63	14.02	22.13
<i>o</i> -Hydroxybenzoate .....	24.52	15.60	18.07	26.10	50.35
<i>m</i> - " .....	16.16	16.52	19.47	18.07	41.84
<i>p</i> - " .....	5.82	10.10	15.16	14.13	12.63

TABLE IV.  
*p*-Hydroxybenzoates.

Lithium.				Rubidium.			
Weight per cent.	Mols. per cent.	Temp.	Solid phase.	Weight per cent.	Mols. per cent.	Temp.	Solid phase.
5.04	0.659	-0.98°	Ice	9.92	0.883	-1.17°	Ice
9.81	1.341	-2.37	"	17.47	1.685	-2.47	"
17.88	2.650	-5.23	"	26.22	2.798	-4.22	"
25.96	4.199	-9.28	"	35.66	4.297	+17.5	1 aq.
31.54	5.488	-12.62*	"	45.95	6.441	45.0	"
30.84	5.280	+12.5	0	55.73	9.248	68.0	"
30.92	5.299	± 0	"	64.95	13.04	94.0	0
31.96	5.557	+85.0	"	74.00	18.72	120.5	"
35.00	6.308	113.0	"	75.92	20.33	127.0	"
Sodium.				Cæsium.			
5.075	0.597	-0.77	Ice	14.34	1.103	-1.56	Ice
10.43	1.293	-2.07	"	20.38	1.677	-2.42	"
19.65	2.678	+7.0	5 aq.	29.57	2.723	-4.27*	"
31.47	4.914	24.0	"	"	"	+3.5	1 aq.
41.32	7.342	36.5	"	40.80	4.395	27.5	"
45.61	8.623	39.0*	"	50.07	6.268	49.0	"
"	"	43.0	0	60.36	9.222	75.5	0
50.51	10.30	107.5	"	65.35	11.17	90.3	"
54.93	12.06	163.0	"	70.67	13.85	107.5	"
Potassium.				73.84	15.84	118.0	"
8.04	0.821	-1.43	Ice	79.88	20.93	136.0	"
15.35	1.848	-3.24	"				
29.91	4.184	+15.8	3 aq.				
35.50	5.355	25.8	"				
45.71	7.932	43.0	"				
56.70	11.82	64.4	"				
59.34	12.99	70.5	"				
63.01	14.84	86.8	0				
64.95	15.94	129.5	"				

\* Metastable point.

The effect of the metal on the formation of hydrates is normal in the benzoates, where only the lithium salt is hydrated; but with the hydroxybenzoates the ordinary rule, that hydration only occurs with the salts of the lighter alkali metals, no longer holds. The cæsium and rubidium salts form hydrates in all cases, in spite of the fact that in the para-series the lithium, and in the meta-series the lithium, sodium, and potassium salts do not. The same relations were found among the alkaline formates, as is described in the preceding paper. It is evident that in the formation of hydrates the kation is not the only determining factor.

Our thanks are due to Mr. T. V. Barker for his kind help in distinguishing crystallographically between the different solid phases.

One of us (E. K. E.) wishes to express her gratitude for a grant from the Department of Scientific and Industrial Research.

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### CCXXIII.—*The Solubility and Volatility of 3:5-Dinitrophenol.*

By NEVIL VINCENT SIDGWICK and THOMAS WESTON JOHNS  
TAYLOR.

IN a previous paper (Sidgwick and Aldous, T., 1921, 119, 1001) these properties have been measured for five of the six possible dinitrophenols. We have now completed this investigation by examining the sixth member of the group, the symmetrical (1:3:5) compound. We have also been able to make a considerable improvement in its preparation.

*Preparation of 3:5-Dinitrophenol.*—The chief method that has hitherto been employed is that described by Lobry de Bruyn (*Rec. trav. chim.*, 1890, 9, 209) and used by Holleman (*ibid.*, 1902, 21, 438). It consists in converting *s*-trinitrobenzene into the dinitroanisole by boiling it with sodium methoxide in methyl-alcoholic solution, and hydrolysing the latter by heating it with concentrated hydrochloric acid in a sealed tube at 180° for six hours. The conversion into the anisole offers no difficulty, but the hydrolysis was found to be unsatisfactory, both on account of the time it takes and because the high temperature that has to be used brings about the formation of much tar. The best yield obtained by this method was 28 per cent. of theory, calculated on the trinitrobenzene. Hydriodic acid was tried instead of hydrochloric acid, but after heating for half an hour at 100° the main product was 3-nitro-5-aminoanisole, m. p. 118°. The removal of the methyl group by the action of aluminium chloride with carbon disulphide or benzene as solvent was also unsatisfactory, especially in the former case. Eventually it was found that the action of dry aluminium chloride in the absence of any solvent gave completely satisfactory results (compare Gattermann and Hartmann, *Ber.*, 1892, 25, 3531). The procedure adopted was as follows.

Dry 3:5-dinitroanisole was heated with twice its weight of dry, finely powdered aluminium chloride in an oil-bath to 120°, and kept at this temperature until the evolution of methyl chloride ceased. The product was treated with crushed ice, and the re-

sulting solution made strongly alkaline, cooled, and filtered. On acidifying and again cooling the filtrate, the dinitrophenol crystallised out. The yield of anhydrous phenol by this method varied from 85 to 90 per cent.; the over-all yield, calculated on the trinitrobenzene used, was 77–80 per cent. of theory.

The phenol thus obtained was purified by repeated crystallisation from very dilute hydrochloric acid. It separates in fine, almost colourless needles, which Holleman (*loc. cit.*) has stated to be a hydrate. It was analysed and shown to have the formula  $C_6H_3(NO_2)_2 \cdot OH, 2H_2O$  by estimation of the nitro-groups by the method of Knecht and Hibbert (*Ber.*, 1903, **36**, 1549) and also by the loss of weight on drying at  $55^\circ$  (Found : loss = 16.41. Calc. for dihydrate, loss = 16.36 per cent.).

The transition temperature of this hydrate (that is, the triple point dihydrate–anhydrous phenol–solution) does not appear clearly from the measurements of the solubility in water, because the solubility at this temperature is small; it was determined by slowly heating a sample of the dihydrate in a sealed bulb and observing the temperature at which it formed a solid and a solution; it was also measured in a dilatometer. These two methods gave concordant results : the transition temperature is  $53.9^\circ$ ,  $0.2^\circ$  below that at which mixtures of the phenol and water break up into two liquid layers.

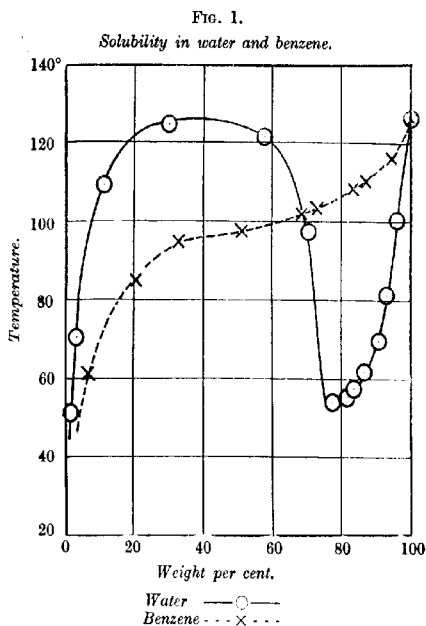
The anhydrous phenol was obtained from the hydrate by heating to  $60^\circ$  in a water-oven, and finally to  $100^\circ$ . The melting point of the pure anhydrous compound was found from a cooling curve to be  $126.1^\circ$  (corr.); Holleman gives  $124^\circ$ .

*Latent Heat of Fusion.*—This was determined by measuring the depression of the freezing point on the addition of benzil, and of *m*-dinitrobenzene. The values obtained were :—

Benzil.			<i>m</i> -Dinitrobenzene.		
Weight per cent. of solute.	Depression.	Heat of fusion.	Weight per cent. of solute.	Depression.	Heat of fusion.
0.26	0.23°	3.15	0.48	0.55°	3.02
1.20	1.07	3.15	1.83	2.02	3.20
1.91	1.71	3.15			Mean 3.11
		Mean 3.15			

The mean value of *Q*, the latent heat, is 3.13 kg.-calories per gram-molecule.

*Solubility in Water and in Benzene.*—These were measured by the synthetic method previously adopted. The thermometers had been compared with a standard, and were corrected for emergent stem. The results are tabulated below, and are shown in Fig. 1.



In the first table, the letters *H* and *P* indicate that the solid hydrate or anhydrous phenol was in contact with the solution; in other cases, the separation was into two liquid layers. In benzene, the second phase was always solid phenol.

#### Solubility in Water.

Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
100	126.1° P	83.64	57.9° P	57.66	121.5°
96.08	100.5° P	81.70	55.5° P	29.98	124.6
93.00	81.3° P	79.57	54.5° P	10.83	109.3
90.71	69.9° P	77.61	54.1° P	3.23	70.4
86.31	61.9° P	69.66	97.6	1.36	51.6 H

Triple point 54.1°. Critical solution temperature 125°.

#### Solubility in Benzene.

Weight per cent.	Mols. per cent.	Temp.	Weight per cent.	Mols. per cent.	Temp.
100	100	126.1°	51.13	30.72	97.7°
94.20	87.32	116.0	32.63	16.27	94.4
83.73	68.58	102.8	20.13	9.65	85.0
73.08	53.53	103.4	6.39	2.81	60.9

*Volatility in Steam.*—This property was measured by the method previously used (T., 1920, 117, 396), the distillate being analysed by reduction with titanous chloride. Under a pressure of 768.5 mm. the distillate was found to contain 0.0055 per cent. by weight of the dinitrophenol, the temperature of the liquid being 101.2°. The partial pressure of the compound in the vapour in equilibrium with the two liquid layers which are present at this temperature is therefore 0.00413 mm. From this we can calculate approximately the vapour pressure of pure liquid dinitrophenol at the same temperature, by the method already explained (Sidgwick and Ewbank, T., 1921, 119, 995). At the triple point, the partial pressure of the phenol above the solution is equal to the vapour pressure of the solid, and the ratio of this to the vapour pressure of the pure liquid can be calculated from the heat of fusion to be 1 : 2.37. The saturated liquid layer at 100° has a composition not very different from that of the triple point, and over this range the vapour pressure changes very slowly with composition. We can therefore assume that the vapour pressure of the liquid is lowered by the dissolved water at 100° in the same ratio as it is at the triple point, in which case the pure liquid has a vapour pressure of  $0.00413 \times 2.37 = 0.0098$  mm.

*Nominal Heats of Solution.*—From the benzene solubility curve, what have in previous papers been called the nominal heats of solution at various concentrations can be calculated by the use of the equation which van't Hoff deduced by means of the osmotic pressure. As it may be doubted how far it is legitimate to make use of osmotic pressure in dealing with concentrated solutions, it is worth pointing out that the same relation can be established without regard to the osmotic pressure, by considering the vapour pressure alone. The whole object of the calculation of the nominal heat of solution is to obtain a measure of the departure of the actual solubility curve (and therefore of the vapour pressure curve) from that given by a normal pair of components. The vapour pressure curve for such a pair is of the simplest possible kind, the partial pressure of each component being equal to the product of its vapour pressure in the pure state into its molecular concentration in the solution. This is not merely an ideal case: many examples are known of systems giving this straight-line curve within the limits of experimental error.\* Hence if  $p$  is the vapour pressure of a pure liquid, and  $p_1$  its partial pressure in the vapour of the solution in which its molecular concentration is  $s$ , we have, for a normal system,

$$p_1 = p \times s \text{ or } s = p_1/p.$$

\* Compare Roozeboom, "Das Heterogene Gleichgewicht," 1904, 2, I, 21; Young, "Distillation Principles and Processes," 1922, p. 30.

This relation must determine the normal form of the solubility curve; and it is easy to show that this curve must give values of the heat of solution calculated by means of the van't Hoff equation, which are constant (or, strictly speaking, which fall slightly with diminishing concentration). The ratio of the vapour pressure of a pure liquid ( $p$ ) to that of the solid ( $p'$ ) at a temperature,  $T$ , which is below the melting point,  $T_0$ , can be shown by the application of the Clausius-Clapeyron equation to be given by

$$\log_e \frac{p'}{p} = -\frac{Q}{R} \cdot \frac{T_0 - T}{T_0 T}.$$

The only assumptions made in the deduction are (1) that the molecular volume of the liquid or solid can be neglected in comparison with that of the vapour, and (2) that the heat of fusion,  $Q$ , is independent of the temperature. As to (1), the pressures we are concerned with being of the order of 1 mm., the molecular volume of the vapour will be some 20,000 litres, whilst that of the liquid or solid is of the order of 100 c.c. As to (2), it has already been shown (Sidgwick and Ewbank, T., 1921, **119**, 993) that  $Q$  will always fall, but seldom more than 30 per cent. for 100° fall of temperature. We may therefore accept the conclusion with this limitation.

Now in a saturated solution of a solid, the partial pressure of this component in the vapour is equal to the vapour pressure of the solid, that is,  $p_1 = p'$ . But we have already seen that, for normal substances,  $s = p_1/p$ . Hence  $s = p'/p$ .

Hence

$$\log_e s = -\frac{Q}{R} \cdot \frac{T_0 - T}{T_0 T},$$

or, if we take the values  $s_1, s_2$  of the solubility at the temperatures  $T_1, T_2$ ,

$$\log_e \frac{s_1}{s_2} = \frac{Q}{R} \cdot \frac{T_1 - T_2}{T_1 T_2}.$$

It follows that this equation, which has hitherto been used for calculating  $Q$ , is always justified when the two components give a normal straight-line vapour pressure curve. This conclusion is, in fact, Raoult's law. If  $Q$  does not remain constant (or fall slightly with diminishing concentration), this indicates that the system is departing from normal behaviour; and if  $Q$  becomes very large (indicating a very slow change of partial pressure with concentration), that is evidence that the system is approaching the temperature at which it separates into two liquids.

The nominal heats of solution of 3:5-dinitrophenol in benzene are given in the following table, and are plotted in Fig. 2, where

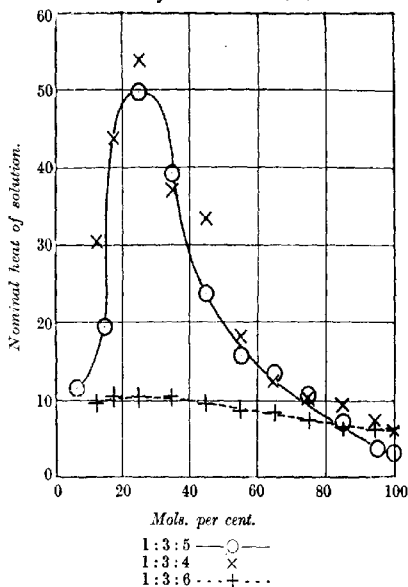


the values for two of the isomeric phenols are added for comparison. In the table, the concentrations are expressed in gram-mols. per 100 gram-mols. of solution, and the heats in kg.-calories. The first value is the latent heat of fusion obtained from the cryoscopic measurements already described.

Nominal Heats of Solution in Benzene.

Mean mol. per cent.	Heat of solution.	Mean mol. per cent.	Heat of solution.
100	3.13	45	23.75
95	3.86	35	39.29
85	7.31	25	49.89
75	10.82	15	19.36
65	13.38	6.5	11.64
55	15.55		

FIG. 2.

*Heats of solution in benzene.*

For comparison, the chief properties of this compound are tabulated below, together with those of two of its isomerides which also have the meta-position occupied, the 1:3:4 and the 1:3:6 or 1:2:5:—

DRUCE: ISOPROPYLSTANNONIC ACID AND ITS DERIVATIVES. 1859

Compound.	1:3:5.	1:3:4.	1:3:6.
Vap. press. at 100° in mm. $\times 100$ {			
obs.	0.413	0.103	44.8
corr.	0.98	0.664	50.6
Crit. sol. temp. in water .....	125°	105.2°	{ v. high (>200°)
Increase of <i>Q</i> in benzene .....	46.7	46.4	4.0

The behaviour of this compound is in complete accordance with the conclusions of the previous work. It belongs to the group which have a low vapour pressure, a low critical solution temperature in water, and a large increase of heat of solution in benzene. These three properties have been shown to be characteristic of those nitrophenols which are not substituted in the ortho-position to the hydroxyl group.

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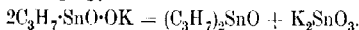
[Received, July 31st, 1922.]

CCXXIV.—*isoPropylstannonic Acid and its Derivatives.*

By JOHN GERALD FREDERICK DRUCE.

*iso*PROPYLSTANNONIC ACID, prepared in a similar manner to ethylstannonic acid \* (T., 1921, 119, 758), by the interaction of *iso*-propyl iodide and potassium hydrogen stannite in accordance with the equation  $C_3H_7I + KHSnO_2 = C_3H_7SnO \cdot OH + KI$ , is amphoteric, forming salts with bases (most of which are basic) and dissolving in hydrochloric or hydrobromic acid to give the tin *iso*propyl trihaloid.

By boiling with excess of alkali hydroxide solution, the acid is converted into diisopropylstannic oxide:



This reaction recalls the mode of formation of ketones, with which this oxide is analogous but to which it shows very little resemblance in physical and chemical properties. When treated with hydrochloric or hydrobromic acid, it yields the corresponding dihaloid.

The di- and tri-haloid derivatives,  $(C_3H_7)_2SnX_2$  and  $C_3H_7 \cdot SnX_3$ , yield double salts with the halogen salts of pyridine. These substances have properties similar to those of the organic stannichlorides (T., 1918, 113, 715).

EXPERIMENTAL.

*isoPropylstannonic Acid*,  $C_3H_7 \cdot SnO \cdot OH$ .—The potassium hydrogen stannite solution required was made by adding a sufficient quantity

\* Called ethylstannic acid in the paper quoted.

(about 250 c.c.) of 10 per cent. potassium hydroxide to produce a clear solution with 20 grams of stannous chloride, shaken with 60 c.c. of water. *iso*Propyl iodide (22 grams) was then added and the mixture was shaken at intervals during ten days.\* When the *iso*propyl iodide had disappeared, the solution was treated with dilute hydrochloric acid until neutral, the gelatinous precipitate of *isopropylstannonic acid* filtered, washed with warm water, and dried on a porous plate (Found: Sn = 59.9; C = 18.0; H = 4.5.  $C_3H_7O_2Sn$  requires Sn = 60.0; C = 18.5; H = 4.1 per cent.).

The *isopropylstannonic acid* was an almost white, amorphous substance, which did not melt, but decomposed when strongly heated, leaving a residue of stannic oxide. The acid was anhydrous, and did not gain in weight on exposure to the air. When heated out of contact with the air, it decomposed, giving off *iso*-propyl alcohol, propylene, and a trace of propane. The residue contained stannous and stannic oxides and also a little carbonaceous matter.

The acid was insoluble in water and organic solvents, but dissolved in dilute mineral acids and in sodium or potassium hydroxide.

The *potassium salt*,  $C_3H_7\cdot SnO\cdot OK$ , was prepared by digesting excess of the acid (5 grams) with 40 c.c. of 10 per cent. potassium hydroxide for several hours on a warm water-bath. After filtration the solution was kept in a desiccator over sulphuric acid until colourless, deliquescent, tabular crystals separated. These were washed with alcohol, drained, and dried between filter-paper (Found: K = 16.9; Sn = 49.6.  $C_3H_7O_2KSn$  requires K = 16.7; Sn = 51.0 per cent.). The salt dissolved readily in water, forming a very alkaline solution which became cloudy on keeping and on warming, owing to hydrolysis. With excess of alkali, the solution remained clear.

The *sodium salt* was isolated in the same way as the potassium salt, which it resembled in its properties (Found: Na = 10.3; Sn = 53.7.  $C_3H_7O_2NaSn$  requires Na = 10.6; Sn = 54.8 per cent.).

Basic calcium, strontium, and barium salts were obtained as white precipitates by adding excess of a solution of sodium or potassium *isopropylstannionate* to solutions of the metal chlorides. On analysis, the products were found to contain excess of the alkaline earth metal, and less tin, hydrogen, and carbon than the normal salt,  $(C_3H_7\cdot SnO_2)_2M$ , would require. Other basic salts of little interest were also obtained.

\* In some experiments the equivalent amount of *iso*propyl bromide was used instead of the iodide, and in others the duration of the reaction was shortened by the addition of alcohol to the reaction mixture, thus making it a nearly homogeneous solution.

*Tin Diisopropyl Oxide*,  $(C_3H_7)_2SnO$ .—This substance was most readily formed by heating under reflux for four hours the reaction mixture obtained in the preparation of isopropylstannonic acid. Carbon dioxide was passed through the pale brown solution, and the white precipitate, which, unlike the stannonic acids, was easily filtered and washed, was dried on porous plate in a desiccator over sulphuric acid and solid sodium hydroxide (Found : Sn = 53.6.  $C_6H_{14}OSn$  requires Sn = 53.8 per cent.).

*Tin diisopropyl oxide* is infusible. When heated in air, it yields stannic oxide. It does not dissolve in water, aqueous solutions of alkalis, or in organic solvents, but is soluble in hot hydrochloric and hydrobromic acids, yielding the corresponding tin diisopropyl dihaloids.

The oxide has also been obtained by boiling isopropylstannonic acid with excess of 10 per cent. potassium hydroxide for half an hour. The residue of tin diisopropyl oxide was isolated as described above.

*Tin isoPropyl Tribromide*,  $C_3H_7\cdot SnBr_3$ .—Very deliquescent, pale yellow, prismatic tablets of this substance were obtained by allowing a solution of 4 grams of isopropylstannonic acid in 25 c.c. of concentrated hydrobromic acid to evaporate in an evacuated desiccator over sodium hydroxide (Found : Sn = 28.7; Br = 58.9.  $C_3H_7Br_3Sn$  requires Br = 59.7; Sn = 29.6 per cent.). It melted at about  $112^\circ$  and was very soluble in water, giving a strongly acid solution. Dry ether did not dissolve it, but it was soluble in the moist solvent, and also in glacial acetic acid; hot benzene and chloroform appeared to dissolve it slightly, but the substance was not recovered in a pure condition on removal of the solvent.

*Pyridine isoPropylstannibromide*,  $C_3H_7\cdot SnBr_3\cdot 2C_5H_5N\cdot 2HBr$ .—Tin isopropyl tribromide (2.5 grams) and pyridine hydrobromide (2 grams) were dissolved together in 50 c.c. of dilute hydrobromic acid. The solution was slightly concentrated on the water-bath, and, on cooling, deposited pale yellow, nacreous plates (Found : Sn = 16.5; Br = 55.9.  $C_{13}H_{19}N_2Br_3Sn$  requires Br = 55.4; Sn = 16.5 per cent.). The substance crystallised unchanged from dilute hydrobromic acid, and did not melt at  $300^\circ$ . It was soluble in water and showed the properties of organic stannichlorides (compare T., 1918, 113, 715).

*Pyridine isoPropylstannichloride*,  $C_3H_7\cdot SnCl_3\cdot 2C_5H_5N\cdot 2HCl$ .—Attempts to isolate tin isopropyl trichloride,  $C_3H_7\cdot SnCl_3$ , from hydrochloric acid solutions of isopropylstannonic acid have been unsuccessful. The double pyridine chloride has, however, been obtained by dissolving 3 grams of isopropylstannonic acid in 25 c.c. of concentrated hydrochloric acid and adding 1.8 grams of pyridine

hydrochloride together with 25 c.c. of water. This solution yielded colourless, sword-shaped crystals, which were recrystallised from dilute hydrochloric acid and dried between filter-paper (Found: Cl = 35.1; Sn = 24.0.  $C_{13}H_{19}N_2Cl_3Sn$  requires Cl = 35.4; Sn = 23.9 per cent.).

*Pyridine isopropylstannichloride* did not melt at  $300^\circ$ ; it dissolved in warm water with slight hydrolysis. The acidified solution gave a yellow precipitate when treated with ammonium sulphide.

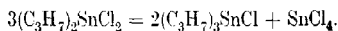
When *isopropylstannonic acid* was acted upon by concentrated hydriodic acid, a clear solution was not obtained. Benzene extracted a pale yellow, crystalline solid from the reaction products. This gave no carbon dioxide or water when ignited with pure copper oxide. The substance melted at  $144^\circ$  and proved to be stannic iodide. Crystals of potassium stanni-iodide,  $K_2SnI_6$ , were obtained when *isopropylstannonic acid* was heated with potassium iodide and hydriodic acid.

With pyridine, the only product of interaction of the acid and hydriodic acid which separated was pyridine tri-iodide,  $C_5H_5N, HI_3$ , in brown needles.

*Tin diisopropyl dichloride*,  $(C_3H_7)_2SnCl_2$ .—Tin diisopropyl oxide (5 grams) was dissolved in 25 c.c. of hot concentrated hydrochloric acid. After cooling in a desiccator, this solution gave almost colourless, transparent crystals, which were recrystallised from benzene, in which they dissolved but sparingly in the cold (Found: Cl = 26.1; Sn = 43.4.  $C_6H_{14}Cl_2Sn$  requires Cl = 25.7; Sn = 43.1 per cent.).

*Tin diisopropyl dichloride* melted at  $80-84^\circ$ , and was soluble in water, alcohol, hot benzene, and hot glacial acetic acid. The chief product of hydrolysis obtained when the aqueous solution was boiled, was the hydroxy-chloride, since, after filtration and washing, it dissolved in hot dilute nitric acid. The solution gave a copious precipitate of silver chloride with silver nitrate solution.

Tin diisopropyl dichloride was deliquescent. When heated, it emitted the strong odour of the tin trialkyl haloids, which suggested that it decomposed in accordance with the equation



This matter is being investigated further.

*Pyridine diisopropylstannichloride*,  $(C_3H_7)_2SnCl_2 \cdot 2C_5H_5N \cdot 2HCl$ .—This double salt was prepared by dissolving together 2 grams of pyridine hydrochloride and 2 grams of tin diisopropyl dichloride in 25 c.c. of hot dilute hydrochloric acid. On cooling, colourless crystals separated (Found: Cl = 28.3; Sn = 24.6.  $C_{16}H_{26}N_2Cl_4Sn$  requires Cl = 28.0; Sn = 23.5 per cent.). The compound began

to darken without melting at  $270^{\circ}$ . It dissolved in water with slight hydrolysis, producing, as in the case of all these double salts, a distinctly acid solution.

*Tin Diisopropyl Dibromide*,  $(C_3H_7)_2SnBr_2$ .—This was obtained by dissolving tin diisopropyl oxide in hot hydrobromic acid. The solution deposited pale yellow, hygroscopic crystals after remaining for several days in a desiccator over solid sodium hydroxide (Found: Br = 43.0; Sn = 31.1.  $C_6H_{14}Br_2Sn$  requires Br = 43.8; Sn = 32.6 per cent.).

*Tin diisopropyl dibromide* decomposed on addition of cold water, in which it dissolved at first. Moist alcohol, acetone, and benzene all dissolved it slightly, but it was insoluble in other organic solvents. It melted at about  $54^{\circ}$ .

*Pyridine Diisopropylstannibromide*,  $(C_3H_7)_2SnBr_2 \cdot 2C_5H_5N \cdot 2HBr$ .—About 2 grams of tin diisopropyl dibromide and 2 grams of pyridine hydrobromide were dissolved together in 20 c.c. of hot dilute hydrobromic acid. The solution deposited very pale yellow platelets (Found: Br = 48.8; Sn = 16.3.  $C_{16}H_{26}N_2Br_4Sn$  requires Br = 49.6; Sn = 16.4 per cent.). The salt dissolved in water with slight hydrolysis. On heating, it began to darken at  $230^{\circ}$  and decomposed at a somewhat higher temperature.

The author wishes to acknowledge his indebtedness to the Chemical Society for a grant from the Research Fund which has largely defrayed the expenses of this investigation.

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BATTERSEA GRAMMAR SCHOOL, S.W.11. [Received, July 18th, 1922.]

### CCXXV.—Piperitone. Part IV. The Interaction of dl-Piperitone and Semicarbazide, and the Isolation of Pure dl-Piperitone.

By JOHN READ and HENRY GEORGE SMITH.

In our original note on the interaction of *dl*-piperitone and semicarbazide (T., 1921, **119**, 784), the effect was described of mixing the ketone in cold aqueous alcoholic solution with an excess of the hydrochloride of the base. The material which separated after a few hours, when once recrystallised from boiling alcohol, melted at  $219$ – $220^{\circ}$ , and seemed to be similar to the semicarbazone of the synthetic  $\Delta^1$ -*p*-menthen-3-one described by Wallach (*Annalen*, 1908, **362**, 272). From the data then at our disposal, the two products appeared, however, to be distinct, owing to apparent

differences in solubility, melting point (Wallach, *loc. cit.*), and ease of formation (compare Roberts, T., 1915, 107, 1466). The lack of reference in these two papers to a benzylidene derivative, which in the case of piperitone is capable of such ready production, seemed to support this conclusion. Unfortunately, also, these sources afforded no reference to hydroxylamine derivatives of the ketones concerned. The question of the identity of piperitone was accordingly reserved for discussion in a later communication, after the accumulation of further data (*loc. cit.*, p. 783).

Subsequently, we were able to obtain access to Schimmel's Semi-Annual Report for October, 1910 (compare Roberts, *loc. cit.*), giving a description (p. 97) of a  $\Delta^1$ -*p*-menthen-3-one from Japanese peppermint oil, which yielded not only a semicarbazone melting at 224–226°, but also an oxime melting at 107–109° and a hydroxylaminoxime melting at 164–165°. The strong case thus established for the acceptance of the chemical identity of piperitone with the ketonic constituent of Schimmel's Japanese peppermint oil and Roberts's oil of *Cymbopogon sennaarensis*, and with Wallach's synthetic ketone, was strengthened in a striking manner by Simonsen's contemporaneous investigation of the dextrorotatory ketone from the oil of the Himalayan grass, *Andropogon Jwarancusa* (T., 1921, 119, 1644). In a more recent communication (this vol., p. 589) this conclusion was confirmed by the establishment of the crystallographic identity of *dl*-piperitone- $\alpha$ -oxime, prepared from the levorotatory ketone of *Eucalyptus dives*, with a corresponding product derived by Simonsen from the dextrorotatory ketone of *A. Jwarancusa*. The additional observation, recorded below, that *dl*-piperitone from *E. dives* yields two semicarbazones, melting after careful purification at 226–227° and 174–176°, respectively, provides a further indication of the chemical identity of the ketones from the various sources which have been mentioned.

Judging from the small, but distinct dextrorotations shown by the preparations, extracted with sodium sulphite solution, from the oils of Japanese peppermint and *C. sennaarensis*, piperitone occurs in these oils, as in that of *A. Jwarancusa*, in the dextrorotatory form. Thus, the ketone isolated by Simonsen from the last-named source by fractional distillation under diminished pressure had  $[\alpha]_D^{20} + 36.76^\circ$ , but after treatment with sodium sulphite and alkali the value for the purified ketone had declined, owing to partial racemisation, to  $[\alpha]_D^{20} + 7.92^\circ$ . Specimens prepared from the oil of *E. dives* by fractional distillation under diminished pressure often exhibit values in the vicinity of  $[\alpha]_D^{20} - 50^\circ$ . It is thus noteworthy that piperitone appears to occur in the dextrogyrate modification in the natural sources known in the Northern

hemisphere,\* whilst in the Southern hemisphere it is the *laevogyrate* modification which is produced (compare this vol., p. 584).

A consideration of the constitution of piperitone in relation to its general chemical behaviour is reserved for a later communication. In the present paper, we are able for the first time to record certain physical constants for pure *dl*-piperitone. The value 46.70, determined for the molecular refractivity, is the highest yet recorded for this substance; the calculated value for a ketone,  $C_{10}H_{16}O$ , with one ethylenic linking is 45.82, the exaltation being therefore 0.88. The physical evidence thus corresponds with conjugation of the two unsaturated groupings, but it is noteworthy that the calculated value of the molecular refractivity for the enolic form of the substance is 46.76. The density of pure *dl*-piperitone is appreciably lower than the values hitherto recorded, the discrepancy amounting to as much as 0.4 per cent. in the case of Wallach's synthetic product. The boiling point of the pure substance, when distilled under atmospheric pressure, is also somewhat lower than the temperatures observed in the investigations to which reference has been made (compare Roberts, *loc. cit.*).

It may be pointed out that no formal proof has yet been adduced of the constitutional identity of the optically active and inactive ketones. Most of the derivatives yet described have been optically inactive, and the possibility of racemisation being accompanied by isomerisation is forming the subject of inquiry. The physical and chemical properties of the optically active ketone are also under investigation.

Although pure benzylidene-*dl*-piperitone is readily prepared from the crude ketone, isolated from the essential oil of *E. dives* by fractional distillation under atmospheric pressure, yet it proved impracticable to obtain a pure semicarbazone directly from material of this kind. In our original communication (*loc. cit.*, p. 781) we ascribed the slight but persistent levorotation shown by specimens of the racemised ketone, isolated from *E. dives*, to contamination with small quantities of a levorotatory impurity. This foreign substance, the identity of which we hope to investigate, appears to form a semicarbazone which is difficult to separate from the semicarbazones of *dl*-piperitone: in an experiment described below, for example, the crude ketone had  $[\alpha]_D^{20} = -0.50^\circ$ , whilst the regenerated specimens from the purified  $\alpha$ - and  $\beta$ -semicarbazones had the respective values  $[\alpha]_D^{20} = -0.13^\circ$  and  $[\alpha]_D^{20} = -1.37^\circ$ . In order to obtain pure *dl*-piperitone, it is therefore necessary to

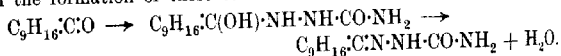
\* The sense of the optical rotation of the  $\Delta^1$ -menthen-3-one reported by Schimmel and Co. to occur in camphor oil is not evident (compare Gilde-meister and Hoffman, "Die ätherischen Öle," Leipzig, 1913, II, 482).



submit the crude ketone to a preliminary purification by the sulphite method before converting it to semicarbazone.

Further investigations on the preparation of *dl*-piperitone-semicarbazones disclosed several points of interest. The reaction between the ketone and semicarbazide hydrochloride takes place fairly readily at the ordinary temperature in aqueous alcoholic solution, and the separation from the acid liquid consists of almost pure  $\alpha$ -semicarbazone; the  $\beta$ -compound appears to be more strongly basic than the  $\alpha$ -compound, since it is not precipitated when the filtrate is diluted with water. On the other hand, by heating an aqueous alcoholic solution of *dl*-piperitone, semicarbazide hydrochloride, and sodium acetate for several hours, the yield of the  $\alpha$ -compound is nearly doubled, the formation of the isomeric substance being almost completely suppressed.

The readiness with which *dl*-piperitone yields a hydroxylaminoxime rendered it of interest to attempt the preparation of a semicarbazido-semicarbazone, particularly in view of the conclusions of Rupe and later investigators concerning the constitutional peculiarities which appear to favour the formation of such derivatives (compare von Auwers, *Ber.*, 1921, 54, [B], 987; Heilbron and Buck, *T.*, 1921, 119, 1515). Although no evidence was forthcoming of the occurrence of such a derivative in this instance, yet in aqueous alkaline mixtures, favouring enolisation of the ketone, very slow reaction ensued, leading to the production of a stable and well-defined additive compound of *dl*-piperitone and semicarbazide. From the behaviour of this substance it appears that the addition is associated with the ketonic group, and not with the ethylenic linking. The new substance, besides being the most distinctive semicarbazide derivative of *dl*-piperitone, is of exceptional interest as establishing a definite intermediate additive stage in the formation of these semicarbazones:



An investigation of the behaviour, under similar conditions, of other ketones and related substances is in progress, and we reserve this field of work.

#### EXPERIMENTAL.

##### *Methods of Preparing the $\alpha$ - and $\beta$ -Semicarbazones of dl-Piperitone.*

1. *dl*-Piperitone (35 grams; 1 mol.) was added to an excess of semicarbazide hydrochloride (30 grams; 1.2 mols.) dissolved in water (120 c.c.), and the homogeneous liquid which resulted upon adding methylated spirit was kept at the ordinary temperature for about two days. The ensuing crystalline deposit, which had formed

to a considerable extent after the lapse of a few hours, when collected, washed with warm alcohol, and dried (16 grams), melted at 226—227°. By diluting the filtrate with water and treating the precipitate in a similar manner, a further small quantity (1.4 grams) of the same substance was obtained. The total yield (17.4 grams) of the  $\alpha$ -semicarbazone was 36 per cent. of the calculated amount.

The addition of a slight excess of ammonia to the aqueous alcoholic filtrate produced a copious precipitate (13.8 grams) of the  $\beta$ -semicarbazone, and evaporation of the filtered liquid gave a little more (2.5 grams) of the same substance. The total yield of the crude  $\beta$ -semicarbazone (16.3 grams) was 34 per cent. of the calculated amount, and after one recrystallisation from alcohol it melted at 174—176°. It possessed a distinct yellow tinge, which was not lessened by repeated crystallisation from alcohol (Found:  $N = 20.3$ .  $C_{11}H_{19}ON_3$  requires  $N = 20.1$  per cent.).

In a similar experiment, the original solution was raised to the boiling point for a short time, after adding the methylated spirit, but the only apparent result was an acceleration of the reaction.

2. Crystallised sodium acetate (41.5 grams) was dissolved in water (50 c.c.) containing an equivalent amount of semicarbazide hydrochloride (30 grams) in solution; *dl*-piperitone (35 grams) was added, and the mixture diluted with warm methylated spirit until the attainment of a clear solution. After two days, the crystalline deposit (18.6 grams) was collected and washed with warm alcohol; it melted at 210° and consisted of a mixture of the  $\alpha$ - and  $\beta$ -semicarbazones, from which almost pure  $\alpha$ -semicarbazone, melting at 225—226°, was obtained after two recrystallisations from acetic acid.

The aqueous alcoholic filtrate from the crude product gave a precipitate when diluted with water; this consisted of a mixture of the  $\alpha$ - and  $\beta$ -semicarbazones, in which the latter compound predominated. The pure  $\beta$ -compound, melting at 174—176°, was obtained after patient recrystallisations from alcohol.

Very similar results were achieved by using acetic acid in place of alcohol in the original reaction mixture.

3. *dl*-Piperitone (65 grams; 1 mol.) was added to a solution in water (66 c.c.) of semicarbazide hydrochloride (54 grams; 1.1 mols.) and sodium acetate (75 grams). Sufficient hot methylated spirit was added to clear the solution, which was then boiled gently under reflux on the water-bath. Separation of semicarbazone began after about two hours, and at the end of six hours the product was transferred to a hot filter, the solid being washed successively with hot methylated spirit, hot water, and hot alcohol. The dry

substance (40 grams) melted at 226—227° and consisted of pure  $\alpha$ -semicarbazone (Found: N = 20.2 per cent.). The filtrate and washings, on evaporation, yielded further amounts of crystalline material, which after purification with hot alcohol proved to be mainly  $\alpha$ -semicarbazone (15 grams), melting at 226—227°. From the mother-liquors was isolated a small quantity (2.4 grams) of the  $\beta$ -semicarbazone melting at 174—176°. The total amount of  $\alpha$ -semicarbazone isolated (55 grams) was 62 per cent. of the theoretical. The yield was not increased by neutralising the filtrate with ammonia.

*Properties of the  $\alpha$ - and  $\beta$ -Semicarbazones of dl-Piperitone.*—dl-Piperitone- $\alpha$ -semicarbazone crystallises in minute, glistening leaflets, which, in bulk, possess a soapy feel. The substance is quite devoid of colour, and melts to a clear, colourless liquid at 226—227°. When heated somewhat above its melting point, it loses ammonia, but does not yield piperitone, the residue consisting of a dark, resinous mass. It is characterised by sparing solubility in most of the ordinary solvents, but it may be crystallised from hot acetic acid or nitrobenzene, a certain amount of decomposition occurring in the latter solvent at temperatures near the boiling point.

The  $\alpha$ -semicarbazone is practically insoluble in cold dilute hydrochloric acid, but it dissolves in the cold concentrated acid, yielding a colourless solution, from which it is reprecipitated on the addition of ammonia or sodium hydroxide solution. It undergoes comparatively slow hydrolysis in hot, strongly acid solutions. Solutions in hot acetic acid show no marked reaction with bromine. The substance forms a clear, colourless solution when suspended in chloroform and submitted to the action of dry hydrogen chloride.

dl-Piperitone- $\beta$ -semicarbazone, when prepared as stated above, forms minute needles, melting at 174—176° to a clear, faintly yellow liquid, which, on cooling, solidifies to a transparent resin. When heated above the melting point, it decomposes slightly, with evolution of ammonia and formation of a pale yellow resin. It is readily soluble in alcohol, chloroform, and other organic solvents, and it dissolves very sparingly in hot water. The crystals exhibit a faint, but distinct yellow tinge, whilst solutions in dilute hydrochloric acid are deep yellow; neutralisation with alkali reprecipitates the original faintly tinged solid. Solutions in chloroform also become deep yellow on treatment with dry hydrogen chloride. The  $\beta$ -semicarbazone is readily hydrolysed by hot dilute hydrochloric acid, yielding piperitone. Bromine does not appear to affect it in hot acetic acid solution.

When prepared from semicarbazido-dl-piperitone, in the manner described below, the  $\beta$ -semicarbazone was quite colourless, and it

melted at 174—176° to a colourless liquid which formed a transparent resin on cooling. Neither preparation appeared to be affected when maintained at 150° for fifteen minutes, and a mixture of the two melted unchanged at 174—176°: the yellow colour thus seems to be due to the presence of traces of an impurity. The yellow specimen was hydrolysed with distinctly greater rapidity than the other, when boiled with dilute hydrochloric acid.

*Semicarbazido-dl-piperitone*,  $C_9H_{16} \cdot C(OH) \cdot NH \cdot NH \cdot CO \cdot NH_2$ .—A mixture of a solution of semicarbazide hydrochloride (5 grams) in water (25 c.c.) with *dl*-piperitone (6.2 grams) was rendered slightly alkaline by the addition of 10 per cent. sodium hydroxide solution and shaken in a stoppered flask at intervals. After keeping overnight, a further quantity of semicarbazide hydrochloride (5 grams) in water (25 c.c.) was added, and the mixture again made alkaline. No sign of reaction was evident for several days, but after keeping for a week, with frequent shaking, a considerable amount of solid material had separated in small, opaque granules, and after the lapse of about three weeks the reaction appeared to be complete.

The product was collected and freed from inorganic impurities and unchanged piperitone by washing with water and ether. The substance was first recrystallised from hot alcohol, in which it was moderately soluble, and finally from hot water, in which it dissolved rather sparingly. It was moderately soluble in chloroform and almost insoluble in ether or benzene. The yield of purified product amounted to about 75 per cent. of the weight of the ketone taken, best results being achieved by the use of small quantities of the reactants (Found: C = 58.2; H = 9.0; N = 19.3.  $C_{11}H_{21}O_2N_3$  requires C = 58.1; H = 9.3; N = 18.5 per cent.).

*Semicarbazido-dl-piperitone* crystallises in colourless, glistening leaflets, which attain a much larger size than the crystals of the semicarbazones of *dl*-piperitone. The substance melts at 186—187°; slightly above this temperature it decomposes with vigorous evolution of ammonia, and at higher temperatures piperitone is regenerated. It dissolves readily in cold dilute hydrochloric acid, and on the addition of ammonia separates slowly from the solution in glistening leaflets. The solution in concentrated hydrochloric acid, when slightly warmed, becomes cloudy, owing to the liberation of piperitone. The ketone is also slowly evolved from the boiling aqueous solution of the derivative.

A suspension of semicarbazido-*dl*-piperitone in chloroform, unlike similar suspensions or solutions of the  $\alpha$ - and  $\beta$ -semicarbazones, readily yielded a colourless precipitate when saturated with dry hydrogen chloride. This substance, which was apparently semi-

*carbazido-dl-piperitone hydrochloride*, melted and decomposed at 165—167°; it was stable in air, and dissolved readily in water and rather sparingly in dilute hydrochloric acid (Found: HCl = 14.4.  $C_{11}H_{21}O_2N_3 \cdot HCl$  requires HCl = 13.8 per cent.). The original base (m. p. 186—187°) was precipitated from the aqueous solution when neutralised with ammonia. The same derivative was produced, in a well-defined crystalline form, by moistening semicarbazido-*dl*-piperitone with concentrated hydrochloric acid; on keeping such a mixture, the crystals soon disappeared, and the resulting solution, when diluted with water after the lapse of an hour, yielded piperitone.

When a solution of semicarbazido-*dl*-piperitone in the least possible quantity of dilute hydrochloric acid was kept for forty-eight hours and then neutralised with ammonia, it yielded a colourless precipitate, consisting of a mixture of the  $\alpha$ - and  $\beta$ -semicarbazones of *dl*-piperitone. The  $\beta$ -derivative, prepared in this manner, was devoid of colour, as noted above (Found: N = 20.1 per cent.). A similar result was attained by mixing aqueous solutions of semicarbazido-*dl*-piperitone and semicarbazido hydrochloride and keeping for the same period, with or without the addition of sodium acetate; no indication was obtained of the formation of a semicarbazido-semicarbazone.

An aqueous solution of semicarbazido-*dl*-piperitone, when heated on the water-bath for two hours with a slight excess of hydroxylamine hydrochloride and sodium acetate, failed to yield an oxime, most of the substance being recovered unchanged.

Solutions of the derivative in warm acetic acid readily underwent oxidation with bromine, yielding carbon dioxide, ammonium bromide, thymol, and other products.

The derivative obtained from *l*-piperitone under the prescribed conditions was identical with the semicarbazido-*dl*-piperitone just described; its saturated alcoholic solution exhibited no measurable optical activity in a 2-dm. tube when examined in sodium light at the ordinary temperature.

*The Preparation of Pure dl-Piperitone.*—In the initial attempt to prepare pure *dl*-piperitone, quantities of the  $\alpha$ - and  $\beta$ -semicarbazones were prepared by method (1), as described above, from a specimen of the ketone isolated from the crude oil of *E. dives* by fractional distillation under atmospheric pressure and having  $[\alpha]_D^{20} = 0.50$ . The ketone was regenerated from each of the semicarbazones by means of steam distillation in the presence of 20 per cent. oxalic acid solution; the two specimens were then separated from the aqueous distillates, dried over calcium chloride, and filtered, but not redistilled. Since both specimens were still distinctly optically

active, they could not be regarded as pure *dl*-piperitone, but certain physical constants were nevertheless determined. The specimen regenerated from the  $\alpha$ -semicarbazone had  $[\alpha]_D^{20} - 0.13^\circ$ ,  $d_4^{20}$  (vac.) 0.9335, and  $n_D^{20}$  1.4848; whilst that from the  $\beta$ -semicarbazone had  $[\alpha]_D^{20} - 1.37^\circ$ , and  $n_D^{20}$  1.4848. Both specimens boiled at 115–116°/20 mm.

Pure *dl*-piperitone was eventually prepared by extracting the crude oil of *E. dives* with sodium bisulphite and converting the ketone from the recrystallised bisulphite compound into the  $\alpha$ -semicarbazone, according to method (3) described above. After the preliminary purification over the bisulphite compound, the ketone\* boiled at 152°/75 mm. and had  $[\alpha]_D^{20} - 3.67^\circ$ . The derived  $\alpha$ -semicarbazone (40 grams, m. p. 226–227°) was boiled under reflux with a 20 per cent. aqueous solution of oxalic acid for thirty minutes, after which the mixture was steam distilled. The separated piperitone, when dried over calcium chloride and filtered (27.9 grams), amounted to about 96 per cent. of the calculated yield. It exhibited no measurable optical activity in a 2-dm. tube, when examined in sodium light at 20°; the density prior to redistillation,  $d_4^{20}$  (vac.) 0.9336, was almost identical with that of the foregoing preparation.

*Physical Properties of Pure dl-Piperitone.*—When distilled under diminished pressure, from an oil-bath maintained at 145–150°, the purified ketone passed over completely at 113°/18 mm., the first few drops of the distillate, which contained traces of water, being collected separately.

Determinations of density (reduced to vacuum) were made as follows:  $d_4^{20}$  0.9331,  $d_4^{25}$  0.9294,  $d_4^{30}$  0.9257.

The further value,  $d_{30}^{20}$  0.9296, stands in satisfactory agreement with the corresponding value,  $d_{30}^{20}$  0.9307, found by Simonsen (*loc. cit.*, p. 650) for a specimen of the ketone from *A. Jwaruncusa* which had been purified by solution in sodium sulphite solution.

The refractive index was determined, at the same three temperatures, in the Abbé instrument:  $n_D^{20}$  1.4845,  $n_D^{25}$  1.4825,  $n_D^{30}$  1.4805. The value of  $R_L$ , calculated from the data determined at 20°, is thus 46.70.

When a specimen of pure *dl*-piperitone was distilled under atmospheric pressure (768.6 mm.), about 25 per cent. passed over at 232–233° (corr.), and by the time 50 per cent. had distilled the temperature had reached 235°. The distillate was colourless, but

\* A similar specimen, having  $[\alpha]_D^{20} - 1.44^\circ$ , boiled at 164°/106 mm. The results of investigation on the extraction of the ketone will be published in due course, but it may be mentioned that the optical activity of specimens purified in this manner is to be attributed to incomplete racemisation.

the odour indicated slight decomposition. The residue had a distinct yellow colour.

Pure *dl*-piperitone is quite colourless, and it does not exhibit the marked tendency of the somewhat impure specimens to become yellow when kept.

The *bisnitroso*-derivative of *dl*-piperitone, obtained in small yield by applying the method of Baeyer and Henrich (*Ber.*, 1895, 28, 654) and keeping the mixture at a low temperature for a day or two, corresponded closely with the description given by Roberts (*loc. cit.*) for the derivative obtained in the same way from the ketonic constituent of the oil of *C. seanaarensis*. It formed colourless crystals which melted at 97–98° and decomposed when kept for several months.

*dl*-Piperitone failed to yield an additive product with hydrogen sulphide, when treated in the manner described by Wallach for carvone (*Annalen*, 1899, 305, 224).

We have pleasure in acknowledging our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of these researches, which are being continued.

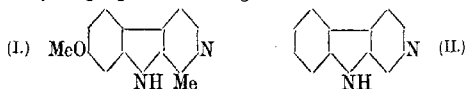
DEPARTMENT OF ORGANIC CHEMISTRY,  
UNIVERSITY OF SYDNEY.

[Received, August 5th, 1922.]

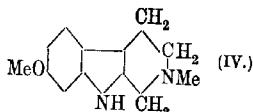
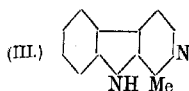
CCXXVI.—*Harmine and Harmaline. Part VI. The Synthesis of N-Methyltetrahydronorharmine and the Constitution of Harmaline and of the Alkylated Harmines.*

By WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, and ROBERT ROBINSON.

It has been clearly shown in the earlier sections of this investigation \* that the analytic evidence which may be brought to bear on the problem of the constitution of harmine indicates that this alkaloid should be represented by the expression I, and the correctness of this view has been confirmed by the syntheses of norharman (II) and of harman (III), which may be derived from the base by simple processes of degradation.

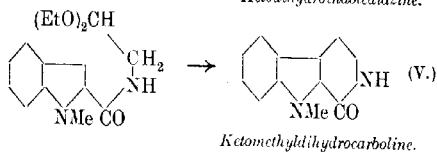
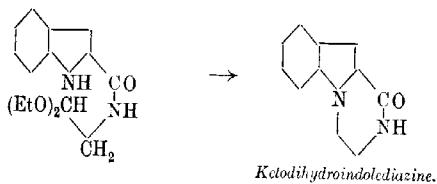


\* Part I, T., 1912, 101, 1775; Part II, T., 1913, 103, 1973; Part III, T., 1919, 115, 933; Part IV, T., 1919, 115, 967; Part V, T., 1921, 119, 1602.



In the present communication, we are able to describe the synthesis of derivatives containing the methoxy-group, the establishment of the position of which by such means removes any possible remaining doubt of the accuracy of the formula which has been put forward as a summary of the reactions of harmine. In order to enable a comparison to be made with the harmine and harman formulae, it may be stated at once that the substance which we have synthesised is *N*-methyltetrahydronorharmine (IV), which may be prepared from either harmine or harmaline by methods detailed in the sequel.

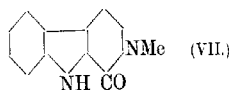
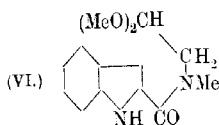
The trinuclear system has been built up by taking advantage of the process developed in connexion with the synthesis of norharman (Part V). Essentially this consists in the ring closure of an acetalylamide of an indole-2-carboxylic acid under the influence of alcoholic hydrochloric acid. The complication which arises from the fact that the elimination of the elements of two molecules of alcohol can occur in two directions is illustrated in the following examples already described in Part V (pp. 1607, 1611).



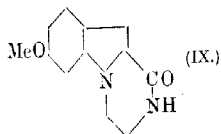
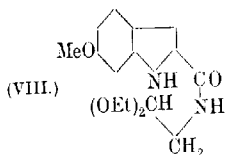
We were thus able to prepare 1-methylcarboline derivatives, and V, on distillation over zinc dust, was converted into norharman. The yield was, however, poor and the purification difficult, and we were very reluctant to contemplate the necessity for the employment of such a method in the synthesis of harmine or norharmine. Moreover, there are grave disadvantages attaching to the application of the zinc dust distillation process to methoxy-compounds, and a



good instance of the anomalous results which may be anticipated is furnished by the work of Irvine and Moodie (T., 1907, **91**, 536) on the nature of the substances obtained by distilling *o*-dimethoxybenzoin over zinc in a stream of hydrogen. In this reduction the main product was *p*-dimethyltolane. In any case it appeared to us that considerable difficulty must be experienced in removing the alkyl group attached to the pyrrole-nitrogen atom, and we therefore attempted the preparation of carboline derivatives from indole-2-carboxyacetylalamides which contain an unsubstituted imino-group in the indole nucleus. The fact that the reactions leading to the indolediazine and carboline types both occurred with facility was encouraging, and our expectation that the balance between the ring closure in the two directions might be a somewhat delicate one was strikingly confirmed by the first modification attempted. Whereas indole-2-carboxyacetylamine gives, as depicted above, an indolediazine, indole-2-carboxydimethylacetyl-methylamide (VI) yields a ketomethylidihydrocarboline (VII) on treatment with alcoholic hydrochloric acid.

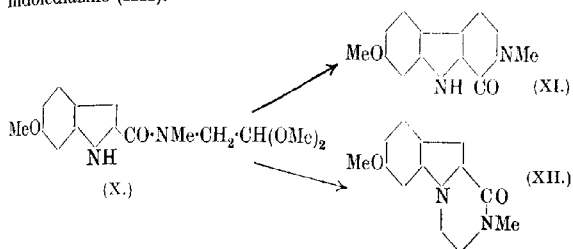


It is very remarkable that such a small constitutional change should so completely alter the course of the reaction and it is difficult to suggest a satisfactory explanation. On distillation over zinc dust in a stream of hydrogen, the new ketomethylidihydrocarboline yields indole and a small amount of norharman. The conversion of 6-methoxyindole-2-carboxyacetylamine (VIII) into the indolediazine derivative (IX) has already been described (Part V, p. 1613), and it was of great interest to determine whether in this series also a carboline would result if the amide nitrogen is alkylated.

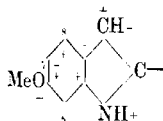


We accordingly prepared 6-methoxyindole-2-carboxydimethylacetyl-methylamide (X) and studied its behaviour towards alcoholic hydrochloric acid. In this case, two substances,  $C_{13}H_{12}O_2N_2$ ,

were isolated and comparison with undoubted indole-diazines and carbolines showed beyond question that, of these, the substance melting at  $246^{\circ}$  is methoxyketomethylidihydrocarboline (XI) and the isomeride melting at  $205^{\circ}$  is methoxyketomethylidihydroindole-diazine (XII).

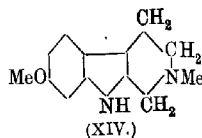
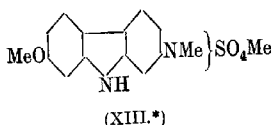


The influence of the methyl attached to the amidic nitrogen is thus again observed, but a comparison with the former example indicates that the methoxyl group has tended to favour the formation of the indole-diazine derivative. This is probably equivalent to the statement that the methoxyl group has activated the hydrogen in position 1 in the indole nucleus to a greater extent than that in position 3. The following scheme illustrates the effect of the negative oxygen atom on the hydrogen atoms in question, and the results observed are seen to be in agreement with the theory of alternate polarity of atoms in a chain.



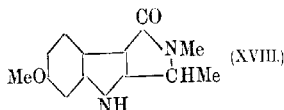
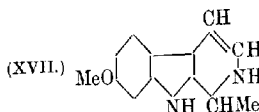
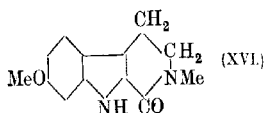
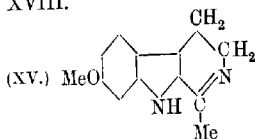
Plainly, methoxyl in position 8 should have a similar effect and facilitate indole-diazine formation, whilst it might be predicted that carboline derivatives should be the main products when the methoxyl is in position 5 or 7.

11-Methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline (XI) yields on reduction with sodium in boiling *n*-butyl alcoholic solution a base,  $C_{13}H_{16}ON_2$ , which, since it may be obtained by applying the same reduction process to norharmine methosulphate (XIII), must be regarded as *N*-methyltetrahydronorharmine (XIV). The identity of the substance prepared by these two methods is a satisfactory proof of the position of the methoxyl group in the molecules of the bases of *Peganum harmala*.



*The Constitution of Harmaline.*

In Part III of this research there was described a neutral substance,  $C_{13}H_{14}O_2N_2$ , m. p.  $228^\circ$ , which results from the oxidation of harmaline methosulphate by means of potassium permanganate in acetone solution, and it was pointed out that, if harmaline has the constitution XV, this substance will be represented by the expression XVI, whilst if the alternative formula XVII be taken for harmaline, the substance, m. p.  $228^\circ$ , must be represented by formula XVIII.



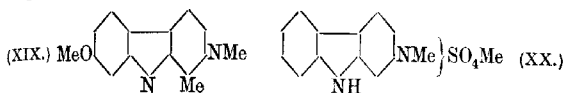
Since, however, the substance, m. p.  $228^\circ$ , yields, on reduction with sodium and *n*-butyl alcohol, *N*-methyltetrahydronorharmine identical with the base obtained as described above, there is no longer any ambiguity, and the oxidation product of harmaline methosulphate must have the constitution symbolised in XVI. Consequently harmaline is represented by the expression XV. Synthetically prepared *N*-methyltetrahydronorharmine has been oxidised by potassium permanganate in acetone solution with

\* The bracket employed in this formula and in similar expressions indicates the salt-like constitution of the substance which is thus symbolised in harmony with Werner's conception of the nature of ammonium and other onium complexes. It is now recognised on all hands that the ionisable bonds (electrovalencies) in salts differ so much, not perhaps in kind but in degree, from the valencies (co-valencies) which occur in typical carbon compounds as to demand a distinctive notation. It may be recalled that the experimental proof of Werner's theory has been furnished by Meisenheimer (*Annalen*, 1913, 397, 273). The plan of using the bracket is not only theoretically sound, but also convenient, as it would be an embarrassment to be forced to decide to which of the nitrogen atoms the chlorine is attached in such substances as methylpropylharmine chloride (formulae XXII and XXIII).

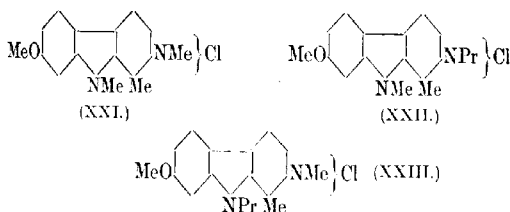
ormation of the substance melting at  $228^{\circ}$ , and this observation is of value inasmuch as it renders possible the proof of identity of a synthetic compound with one prepared from harmaline.

*The Constitution of Alkylated Harmine Derivatives.*

It has already been suggested (Part III, p. 942) that the salt-forming nitrogen atom in the harmine derivatives is that which is situated in the pyridine nucleus, and the formula XIX was assigned to methylharmine. On a similar assumption, norharman methosulphate would be represented by the expression XX.

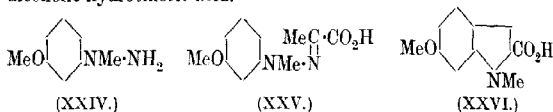


So far as the position of the methyl group is concerned, this hypothesis now receives definite experimental proof, since we have found that norharman methosulphate, on oxidation with potassium ferricyanide in alkaline solution, yields the ketomethyldihydro-carboline (VII), the synthesis of which is mentioned above. The further alkylation of methylharmine should, on the basis of our views, occur at the indole-nitrogen atom and dimethylharmine chloride should be constituted as shown in formula XXI. In order to obtain evidence in support of this theory, we have prepared isomeric methylpropylharmine chlorides by introducing the alkyl groups in a different order. The action of methyl iodide on propylharmine followed by conversion to the chloride by means of silver chloride yields the salt XXII, which closely resembles, but is not identical with, the isomeride (XXIII) prepared from methylharmine and propyl iodide followed by treatment of the product with silver chloride.



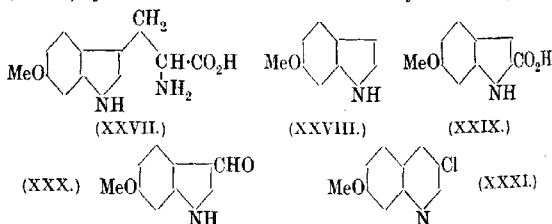
Before we were acquainted with the remarkable effect of the substitution of methyl for hydrogen in the  $\text{—CO—NH—}$  group of indole-2-carboxyacetyl amides on the direction of closing the ring, it seemed that dimethylharmine chloride was a very suitable object of a synthetical investigation, and a plan of attack was

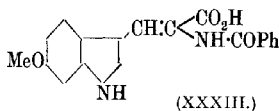
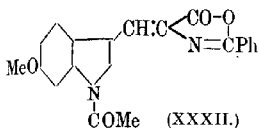
formulated in Part V (p. 1613). The necessary starting point, namely, 6-methoxy-1-methylindole-2-carboxylic acid (XXVI), has been prepared, but, in view of the interesting developments set out above which have enabled our goal to be reached in another way, the further stages of the synthesis have not yet been attempted. *m*-Anisidine was methylated by means of methyl iodide, and the crude methyl-*m*-anisidine directly converted into a nitroso-derivative, which was reduced to *m*-methoxyphenylmethylhydrazine (XXIV) by means of zinc dust in glacial acetic acid solution below 10°. This was readily converted into pyruvic acid *m*-methoxyphenylmethylhydrazone (XXV), but no little difficulty was experienced in inducing the indole transformation until it was found that the reaction proceeded smoothly when the hydrazine was dissolved in saturated alcoholic hydrochloric acid.



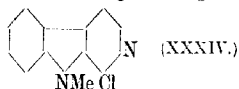
That the indole ring is closed in the *p*-position to the methoxyl group is rendered very probable by a consideration of the behaviour of hydrazones derived from *m*-methoxyphenylhydrazine, which we have already proved yield 6-methoxyindole derivatives (Part V, p. 1614).

We have already shown (Part V, p. 1617) that harman (III) may be obtained from tryptophan by condensation with acetaldehyde followed by oxidation of the product, and it is obvious that if methoxytryptophan (XXVII) could be obtained it should be converted into harmine in a similar manner. Some progress has been made in this direction and the indications that this synthesis is possible are unmistakable (see p. 1884), but the experimental work involved is very tedious and consumes so much time, labour, and expensive material that the investigation has not yet been brought to a conclusion. The starting point was 6-methoxyindole (XXVIII), which was prepared from 6-methoxyindole-2-carboxylic acid (XXIX) by a modification of the method already described (Part V,





p. 1632). 6-Methoxyindole was transformed into 6-methoxyindole-3-aldehyde (XXX) and 3-chloro-7-methoxyquinoline (XXXI) by the action of chloroform and potassium hydroxide in aqueous alcoholic solution. This interesting aldehyde was then condensed with hippuric acid in presence of dry sodium acetate and acetic anhydride, and the lactone (XXXII) thus produced at once hydrolysed by means of aqueous sodium hydroxide with formation of  $\alpha$ -benzoylamino- $\beta$ -[6-methoxyindyl(3)]-acrylic acid (XXXIII). On reduction, hydrolysis, condensation with acetaldehyde, and oxidation, a minute amount of a base which is probably harmine was isolated, but the quantity obtained was insufficient to establish this important result with certainty (p. 1884). An account of the behaviour of some of the substances now described on treatment with magnesium methyl iodide is reserved for a future communication. It may be mentioned here, however, that 3-chloro-1-methyl-4-carboline (XXXIV), which may be prepared under closely defined conditions from 3-keto-1-methyl-3:4-dihydro-4-carboline (V) by the action of phosphorus pentachloride and phosphoryl chloride, does not appear to react with the Grignard reagent.



#### EXPERIMENTAL.

##### 6-Methoxyindole (Formula XXVIII).

It was mentioned in Part V of this research (p. 1632) that some 6-methoxyindole had been obtained by the action of heat on 6-methoxyindole-2-carboxylic acid, but the yield was small and we have since found that the following modification, which consists in decomposing the ammonium salt in the place of the free acid, gives much better results. The dry ammonium salt of the acid (*loc. cit.*, p. 1632), in quantities of 5 grams, contained in a boiling-tube fitted with a spiral glass condenser to the end of which a test-tube is attached, is gradually heated with a small flame. The salt melts and effervesces and when decomposition is complete any sublimate of methoxyindole and ammonium carbonate is washed into the boiling tube with a little hot water, alcohol is added, and the whole heated to boiling, when all dissolves except a small quantity of a

black tar. The liquid is decanted and, on cooling, deposits crude 6-methoxyindole (88 per cent. of theory), which is collected, dried in a vacuum desiccator, and crystallised from light petroleum, from which it separates in plates melting at 91–92°. The yield of pure substance is about 55 per cent. of that theoretically possible.

The *picrate* separated in red needles when solutions of the indole and picric acid in benzene were mixed and was purified for analysis by recrystallisation from benzene containing a little light petroleum, from which the derivative separated in brilliant red needles melting at 137° [Found: N = 15.0.  $C_9H_9ON, C_6H_2(OH)(NO_2)_3$  requires N = 14.9 per cent.].

*6-Methoxy-1-methylindole-2-carboxylic Acid* (Formula XXVI).

The interest attaching to this acid is discussed in the introduction to the present communication (p. 1877; compare also Part V, p. 1613) and the method of synthesis is also sketched. The experimental details of the various stages in the synthesis are as follows:

I. *Preparation of Methyl-m-anisidine*,  $MeO \cdot C_6H_4 \cdot NHMe$ .—In preparing this substance, *m*-anisidine (30.8 grams), contained in a flask connected with a reflux condenser, was mixed in the cold with methyl iodide (39 grams), when the temperature gradually rose and in a short time a vigorous reaction set in. When this had subsided, the semi-solid mass was heated on the steam-bath for several hours, mixed with water and dilute sodium hydroxide, and extracted with ether. The ethereal solution, dried over potassium carbonate, was evaporated and the residue fractionated under reduced pressure, when 32.3 grams distilled at 133–135°/12 mm. as a colourless liquid which doubtless consisted of methyl-*m*-anisidine mixed with unchanged *m*-anisidine and some of the dimethyl derivative.

This oil (7.2 grams) was added to a mixture of ice (20 grams) and concentrated hydrochloric acid (8 c.c.), and sodium nitrite (4 grams) dissolved in water (12 c.c.) run in drop by drop during half an hour, the whole being well cooled all the time. The product, which should just react with starch-potassium iodide paper, was extracted three times with ether, the ethereal solution dried over calcium chloride and evaporated in a weighed flask, when 4 grams of crude nitrosomethyl-*m*-anisidine remained as a dark syrup.

II. *m-Methoxyphenylmethylhydrazine*,  $MeO \cdot C_6H_4 \cdot NMe \cdot NH_2$ .—This substance was prepared by slowly adding the solution of crude nitrosomethyl-*m*-anisidine (4 grams) in glacial acetic acid (8 c.c.) to a well-stirred mixture of zinc dust (16 grams) and water (28 c.c.), the temperature being kept below 10°. The product was kept over-night, again well stirred, and heated on the steam-bath for a few minutes, filtered, the filtrate made alkaline with sodium

hydroxide and extracted several times with ether. This extract, as well as the washings of the zinc dust with ether, was dried over potassium carbonate and the ether distilled off, when crude *m*-methoxyphenylmethylhydrazine (3 grams) remained as a pale brown syrup and was sufficiently pure for the next step.

III. *Pyruvic Acid m-Methoxyphenylmethylhydrazone* (Formula XXV) and (6 ?)-*Methoxy-1-methylindole-2-carboxylic Acid* (Formula XXVI).—When crude *m*-methoxyphenylmethylhydrazine (3 grams) was dissolved in acetic acid (30 c.c. of 15 per cent.) and then pyruvic acid (4 grams) added, a yellow oil separated, which, on standing and rubbing, solidified. After remaining over-night, the crystalline mass was collected, dried in a vacuum, and crystallised from light petroleum, from which *pyruvic acid m-methoxyphenylmethylhydrazone* separated in lemon-yellow needles melting at 66° (Found : C = 59·7; H = 6·5.  $C_{11}H_{14}O_3N_2$  requires C = 59·5; H = 6·3 per cent.). This hydrazone dissolves in sodium carbonate to a deep orange solution and on acidifying with hydrochloric acid, the colour changes to yellow and then rapidly fades owing no doubt to hydrolysis.

After a number of experiments on the action of aqueous hydrochloric acid under different conditions on this hydrazone, during which varying quantities of (6 ?)-methoxy-1-methylindole-2-carboxylic acid, mixed generally with a red amorphous substance completely soluble in glacial acetic acid, were isolated, the following satisfactory process for the preparation of this acid was developed. The *m*-methoxyphenylmethylhydrazone of pyruvic acid was added to about ten times its weight of a saturated alcoholic solution of hydrogen chloride, when it quickly dissolved to a pale red solution and in a minute or two, crystals commenced to separate and the temperature rose considerably. After an hour, the crystals were collected, washed with alcohol, then with water, again with alcohol, and dried in a vacuum desiccator. The acid is sparingly soluble in alcohol and separates in small, stout needles with pointed ends (Found : C = 64·5; H = 5·5.  $C_{11}H_{11}O_3N$  requires C = 64·4; H = 5·4 per cent.). (6 ?)-*Methoxy-1-methylindole-2-carboxylic acid* decomposes at about 235° with evolution of gas. It gives, in alcoholic solution with *p*-dimethylaminobenzaldehyde and hydrochloric acid, a purple solution which fades on boiling. A small quantity of the acid was cautiously heated until decomposition was complete, and the residue dissolved in boiling water; the filtered solution deposited, on cooling, an oil which is evidently the corresponding methoxy-methylindole. In aqueous solution this substance gives with *p*-dimethylaminobenzaldehyde and hydrochloric acid (Ehrlich's reagent) \* a red coloration which becomes intense on the addition

\* This reagent was made by adding concentrated hydrochloric acid (20 c.c.) to the solution of *p*-dimethylaminobenzaldehyde (1 gram) in alcohol (119 c.c.).



of sodium nitrite and shows a strong absorption band in the yellow end of the green. With a pine shaving, a purple reaction is obtained. The addition of a solution of picric acid in benzene to the solution of methoxymethylindole in the same solvent, causes a well-defined *picrate* to separate in red-brown needles which melt at 123°.

6-Methoxyindole-3-aldehyde (Formula XXX) and 3-Chloro-7-methoxyquinoline (Formula XXXI).

These substances were obtained from 6-methoxyindole by treatment with chloroform and potassium hydroxide substantially under the conditions recommended by Ellinger (*Ber.*, 1906, **39**, 2520) for the preparation of indole-3-aldehyde and 3-chloroquinoline from indole. In a flask attached to a reflux condenser and fitted with a stirrer and dropping funnel, 6-methoxyindole (10 grams) is mixed with alcohol (100 c.c. of 96 per cent.), water (20 c.c.), and chloroform (36 c.c.), and the whole heated on the steam-bath just to boiling. Potassium hydroxide (25 grams), dissolved in water (25 c.c.) and made up to 250 c.c. with alcohol (96 per cent.), is dropped in continuously during two and a half hours, the whole being very vigorously stirred. The product is boiled for half an hour, the alcohol and chloroform are distilled off, and the residue is distilled in steam until the distillate gives hardly any coloration on the addition of dilute nitric acid and sodium nitrite. The hot liquid in the flask is quickly filtered and allowed to cool over-night, when 6-methoxyindole-3-aldehyde (0.8 gram) separates in brown needles and, after recrystallisation from water with the aid of animal charcoal, the aldehyde is obtained in almost colourless needles (Found: C = 68.3; H = 5.1; N = 8.0.  $C_{10}H_9ON$  requires C = 68.5; H = 5.1; N = 8.0 per cent.). 6-Methoxyindole-3-aldehyde melts at 185° and gives with sulphuric acid a red coloration due probably to the formation of a dyestuff similar to that observed by Ellinger to be formed under the same conditions from indole-3-aldehyde.

3-Chloro-7-methoxyquinoline.—This interesting substance passes over along with unchanged methoxyindole when the product of the action of chloroform and potassium hydroxide on the latter is distilled in steam as described above. The distillate, which may amount to several litres, is extracted four times with ether, the ethereal solution thoroughly shaken with several small quantities of dilute hydrochloric acid (20 per cent.), dried, and evaporated, when 6-methoxyindole (about 7 grams) remains in an almost pure condition. The acid extract is made alkaline with sodium hydroxide, and air passed to remove the dissolved ether, when needles of the chloromethoxyquinoline soon commence to separate. After some hours, the needles (1 gram) are collected, washed, and recrystallised

from a large amount of boiling water (Found: N = 7.5; Cl = 18.1.  $C_{10}H_9ONCl$  requires N = 7.2; Cl = 18.3 per cent.).

3-Chloro-7-methoxyquinoline melts at 91°, has a curious odour somewhat resembling that of anethole, and is readily soluble in dilute acids. The solution in dilute sulphuric acid, but not in hydrochloric acid, has a strong blue fluorescence, and the addition of hydrochloric acid to the sulphuric acid solution destroys this fluorescence.

The chlorine atom is very firmly fixed, since, after heating with concentrated aqueous ammonia in a sealed tube at 100° for five hours, the substance is recovered unchanged.

*α-Benzoylamino-β-[6-methoxyindyl(3)]-acrylic Acid*  
(Formula XXXIII).

The anhydride of this substance is obtained when 6-methoxy-indole-3-aldehyde is condensed with hippuric acid (compare Ellinger and Flamand, *Ber.*, 1907, 40, 3031). The aldehyde (1 gram), hippuric acid (1.4 grams), and freshly fused sodium acetate (0.55 gram) are finely ground, mixed with freshly distilled acetic anhydride (2.5 c.c.), and heated in a test-tube in a boiling-water bath for fifteen minutes with occasional stirring, care being taken to exclude moisture. The mixture becomes liquid and dark red and, after cooling, the viscous mass is rubbed with warm water and then boiled with water (200 c.c.) and filtered hot; the brittle residue is again ground and extracted with boiling water (100 c.c.). The residual crude az-lactone was not recrystallised, but at once hydrolysed by boiling the finely divided substance with sodium hydroxide (100 c.c. of 1 per cent.) until the odour of ammonia could not be detected. After the addition of dilute hydrochloric acid until the reaction was just acid to Congo-paper, and standing over-night, the precipitate was collected and recrystallised from dilute alcohol, from which it separated in brown-yellow needles. Analysis showed that this substance is benzoylamino(methoxyindyl)acrylic acid (Found: C = 67.3; H = 4.8.  $C_{19}H_{16}O_4N_2$  requires C = 67.8; H = 4.8 per cent.). This substance softens at 215°, melts with decomposition at 230°, and is insoluble in water, but readily so in alcohol; it dissolves in acetic anhydride, and on boiling a red colour develops presumably due to regeneration of the az-lactone.

This acid was reduced in aqueous solution by means of a large excess of sodium amalgam, and the strongly alkaline solution then boiled for ten minutes. The liquid was acidified with dilute sulphuric acid, and a little acetaldehyde added while still hot. This resulted in the formation of a cloud, and condensation obviously occurred. Excess of 5 per cent. potassium dichromate was then

added and the solution boiled and rendered strongly alkaline. The base, if any, was extracted by means of ethyl acetate, and the separated ethyl acetate solution washed with dilute hydrochloric acid. This solution exhibited a blue fluorescence, but nothing could be isolated from it. A more definite result was obtained by reducing the acid in acetic acid solution by shaking with hydrogen after the addition of palladium chloride and gum arabic. After boiling and cooling, the solution was diluted, filtered, and evaporated to dryness in a vacuum. Alcoholic barium hydroxide was added and the solution boiled during an hour, then diluted, rendered just acid with sulphuric acid, and two drops of acetaldehyde added. After heating on the steam-bath for about thirty seconds, a large excess of 5 per cent. potassium dichromate was added and the solution boiled. Sodium hydroxide in excess was then added and the mixture extracted with much ethyl acetate. The filtered extract was shaken with dilute hydrochloric acid, and the strongly fluorescent aqueous solution evaporated to a small bulk. On rendering alkaline, there was a small precipitate, and this was collected and dissolved in methyl alcohol. The solution was concentrated and deposited, on cooling, a minute amount of needle crystals resembling harmine in appearance. These melted at 220–230° and were obviously impure, but mixed with harmine, the melting point was raised to 225–245°. Pure harmine melts at 257°, and it is unfortunate that the amount of base obtained in this experiment did not admit of repeated crystallisation. We have no doubt that this substance consisted of impure harmine, and the fluorescence in acid solution was identical with that exhibited by harmine salts.

### 3-Chloro-1-methyl-4-carboline (Formula XXXIV).

This substance is obtained when 3-keto-1-methyl-3:4-dihydro-4-carboline (m. p. 242°; compare Part V, p. 1638) is treated with phosphorus oxychloride and pentachloride. Unless special conditions are observed, the yield is poor, and experience has shown that the essential points to be observed are that the phosphorus pentachloride is pure and dry, that the oxychloride is distilled immediately before use, and the carboline should be as pure as possible. It is also important that excess of pentachloride should be avoided. The carboline (0.5 gram) \* is mixed in a tube with the oxychloride (6 grams) and then the pentachloride (1 gram)

\* A peculiar characteristic of this substance may be mentioned. It is almost insoluble in water and very sparingly soluble in absolute alcohol, but it dissolves much more readily in alcohol containing water. It separates from water or alcohol in long needles, but from a mixture of alcohol and water in glistening plates.

added. The whole is well stirred, the tube sealed, and heated in the boiling-water bath for six hours. The contents of the tube are poured on to ice and after the oxychloride has been completely decomposed, the solid is collected, washed with dilute ammonia, dried, and recrystallised from light petroleum (b. p. 80–100°) containing some benzene, from which the substance separates in colourless needles (Found: C = 66.2; H = 4.1.  $C_{12}H_9N_2Cl$  requires C = 66.6; H = 4.1 per cent.).

3-Chloro-1-methyl-4-carboline melts at 110°, and is feebly basic, since it yields with concentrated hydrochloric acid a rather sparingly soluble, yellow hydrochloride, which is dissociated by water. The acid solutions do not fluoresce. When the solution in benzene is mixed with a solution of picric acid in the same solvent, a yellow, crystalline picrate separates which melts at 213°. Attempts were made to convert this substance into methyl harman by the action of magnesium methyl iodide in boiling *isoamyl* ether solution, but the only product isolated was keto-1-methyldihydro-4-carboline (m. p. 242°). There is no doubt that a little methylharman is produced, as the acid washings of the *isoamyl* ethereal solution, obtained on adding water to the reaction mixture, exhibited violet fluorescence. The actual amount of the base must, however, be very small.

*Action of Methylamine on Bromodimethylacetal. Formation of Methylaminodimethylacetal,  $NHMe \cdot CH_2 \cdot CH(OMe)_2$ , and Methylaminobisdimethylacetal,  $NMe[CH_2 \cdot CH(OMe)_2]_2$ .*

The researches of Freundler and Ledru (*Compt. rend.*, 1905, 140, 794; *Bull. Soc. chim.*, 1907, [iv], 1, 71) on the action of alcohols on the product of the bromination of paraldehyde have rendered the bromoacetals, and indirectly the aminoacetals, readily accessible substances. Thus, for example, methylaminodimethylacetal results from the action of methylamine on bromodimethylacetal, and as this substance does not appear to have been described and we required it in considerable quantity for the present investigation, we have worked out the following method for its preparation. Bromodimethylacetal (150 grams) is mixed with methyl alcohol (400 c.c.) in which the methylamine obtained by heating 500 grams of the *pure* hydrochloride with concentrated aqueous potassium hydroxide has been absorbed, and the whole heated in an autoclave at 140° for twelve hours. The methyl alcohol and excess of methylamine are distilled off under 200 mm. pressure and used in a subsequent preparation, an equal volume of water is added to the syrupy residue, and the solution, which contains no unchanged bromodimethylacetal, is mixed with a large excess of anhydrous potassium

carbonate and extracted four times with much ether. The ethereal solution, thoroughly dried over potassium carbonate, is evaporated and the residue (85 grams) quickly distilled under 10 mm. pressure, all below  $100^{\circ}$  being collected (the residue [A] is described below).

On fractionating the distillate at the ordinary pressure, methylaminodimethylacetal is readily obtained pure as a limpid oil which has an odour resembling, but more pungent than, that of aminoacetal, and distils at  $140^{\circ}/760$  mm. (Found:  $N = 11.9$ .  $C_5H_{13}O_2N$  requires  $N = 11.8$  per cent.).

The fraction of higher b. p. (A) was collected from several experiments and fractionated under reduced pressure, when the main portion distilled at  $100\text{--}105^{\circ}/10$  mm. as a rather viscid, colourless oil and evidently consisted of *methylaminobisdimethylacetal* (Found:  $N = 6.9$ .  $C_9H_{21}O_4N$  requires  $N = 6.7$  per cent.).

Aminodimethylacetal,  $NH_2 \cdot CH_2 \cdot CH(OMe)_2$  (b. p.  $135^{\circ}/755$  mm.) and aminobisdimethylacetal,  $NH[CH_2 \cdot CH(OMe)_2]_2$  (b. p.  $163^{\circ}/84$  mm.) are readily obtained by heating bromodimethylacetal (150 grams) in an autoclave with alcohol (500 c.c.) which has been saturated with ammonia at  $0^{\circ}$  for ten hours. In working up the product, care must be taken to saturate thoroughly the residue, after distilling off the alcohol and ammonia, with potassium carbonate and to extract several times with much ether, otherwise much of the aminodimethylacetal may be lost. As these aminodimethylacetals are somewhat volatile in ether vapour, the ether used for extractions should be employed in subsequent preparations.

### 3-Keto-4-methyl-3 : 4-dihydro-4-carboline (Formula VII).\*

In the preparation of this substance from indole-2-carboxylic acid, the chloride of the acid was first made by the action of phosphorus pentachlorine on the suspension of the acid in acetyl chloride, and the solution of the acid chloride in chloroform then treated with methylaminodimethylacetal,  $NHMe \cdot CH_2 \cdot CH(OMe)_2$  (compare Part V, p. 1626). After the chloroform had been removed by evaporation, water was added, when an oil separated which soon crystallised. The solid was collected, dried on porous porcelain in a vacuum desiccator, and recrystallised twice from a mixture of benzene and light petroleum, from which colourless needles of *indole-2-carboxydimethylacetyl methylamide* separated; these melted at  $104^{\circ}$  (Found:  $C = 64.3$ ;  $H = 7.0$ ;  $N = 10.6$ .  $C_{14}H_{13}O_3N_2$  requires  $C = 64.1$ ;  $H = 6.9$ ;  $N = 10.7$  per cent.). In order to close the ring, this substance was added to a saturated alcoholic

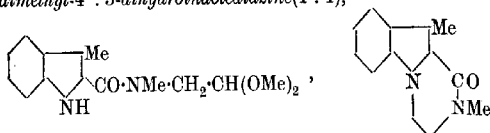
\* In strict accordance with the nomenclature suggested in Part IV (p. 950) for carboline derivatives, the substance described in Part V (p. 1638) as 2-keto-1-methyl-2 : 3-dihydro-4-carboline should have been named 3-keto-1-methyl-3 : 4-dihydro-4-carboline,

solution of hydrogen chloride at 40°, when a clear solution resulted, from which, especially if seeded, crystals of the hydrochloride of ketomethyldihydrocarboline soon began to separate. On the addition of water, a white precipitate was produced, which was collected, washed with water, then with dilute ammonia, and dried; in this condition the substance melts at about 240—255° and yields a green colour with Ehrlich's reagent (p. 1881) which deepens on heating and becomes almost colourless on cooling. After twice crystallising from alcohol, the long, white needles melt at 263° and no longer give this reaction (Found: C = 64.3; H = 7.0; N = 10.6.  $C_{14}H_{15}O_3N_2$  requires C = 64.1; H = 6.9; N = 10.7 per cent.).

3-Keto-4-methyl-3 : 4-dihydro-4-carboline combines with hydrochloric acid to yield a colourless hydrochloride, the solution of which exhibits a faint though perfectly distinct fluorescence. A trace of the substance, heated with zinc dust in a narrow test-tube, gives a sublimate, the solution of which in dilute hydrochloric acid exhibits a marked blue fluorescence. These properties indicate that ring formation in the case of indole-2-carboxydimethylacetalylmethylamide has resulted in the formation of the carboline and not of 5-keto-4 : 5-dihydroindolediazine(1 : 4) (compare p. 1874, and also Part V, p. 1627). It is of considerable interest (see p. 1877) that this substance may be prepared from norharman (Part V, p. 1619) in the following manner. Norharman (0.5 gram), dissolved in boiling benzene (10 c.c.), was converted into its methosulphate by the addition of dry methyl sulphate (1 c.c.) by boiling the solution during an hour. The derivative separated in a crystalline condition and the benzene was decanted. The residue was then dissolved in water (50 c.c.), rendered just alkaline by the addition of potassium hydroxide and heated on the steam-bath. A solution of potassium ferricyanide was then cautiously added until ferricyanide remained in excess. A colourless substance separated in needles and, after cooling, this was collected and crystallised from alcohol. It was obtained in slender needles melting at 263° alone or mixed with synthetic 3-keto-4-methyl-3 : 4-dihydro-4-carboline obtained as described above.

On distillation over a large excess of zinc dust in a stream of hydrogen, a crystalline distillate was obtained. This consisted chiefly of indole, but was found to contain a little norharman. The product was extracted with dilute acid and the picrate prepared. After several crystallisations, a minute amount of material, crystallising from hot water in woolly yellow needles, decomposing at 260°, was obtained. The substance thus appeared to be identical with norharman picrate, and it should also be noted that the acid solution of the base exhibited intense blue fluorescence.

*3-Methylindole-2-carboxydimethylacetalmethylamide and 5-Keto-4 : 7-dimethyl-4 : 5-dihydroindole-diazine(1 : 4),*



3-Methylindole-2-carboxylic acid (scatole-2-carboxylic acid (see Part V, p. 1634) was converted into the acid chloride by means of phosphorus pentachloride and acetyl chloride, and this, dissolved in chloroform, treated with methylaminodimethylacetal (compare Part V, p. 1626). On adding water, an oil separated which, especially when vigorously rubbed, gradually solidified. This crude 3-methylindole-2-carboxydimethylacetalmethylamide was collected, dried on porous porcelain, and crystallised first from a mixture of benzene and light petroleum and then from light petroleum alone, from which it separated in small, flat plates which melt at 87–88° and are readily soluble in most of the usual organic solvents (Found: C = 65.2; H = 7.2; N = 10.0.  $C_{15}H_{30}O_2N_2$  requires C = 65.2; H = 7.2; N = 10.1 per cent.).

When this substance was added to a saturated alcoholic solution of hydrogen chloride at 40°, it dissolved and yellow crystals soon commenced to separate which, after some hours, were collected and recrystallised first from alcohol containing a little ammonia and then from alcohol alone, from which 5-keto-4 : 7-dimethyl-4 : 5-dihydroindole-diazine(1 : 4) separated in long, flat needles melting at 159° (Found: C = 73.6; H = 5.7; N = 13.2.  $C_{13}H_{12}ON_2$  requires C = 73.7; H = 5.7; N = 13.2 per cent.).

In appearance and properties, this substance closely resembles 7-methyl-4 : 5-dihydroindole-diazine(1 : 4) (see Part V, p. 1635). Concentrated hydrochloric acid converts it into a yellow crystalline hydrochloride, which is somewhat soluble in hydrochloric acid to a yellow solution exhibiting no fluorescence, although the neutral or alkaline solutions of the base have a slight blue fluorescence.

On distillation with zinc dust, it develops an odour resembling that of indole and yields a yellow base which has not been further investigated; in this respect it behaves very much like 5-keto-4 : 5-dihydroindole-diazine(1 : 4), which in these circumstances yields indole and an orange base (Part V, p. 1628). On boiling with Ehrlich's reagent (p. 1881), a bluish-green coloration is obtained which almost disappears on cooling, and on warming with vanillin and concentrated hydrochloric acid, a deep purple colour rapidly develops and remains on dilution with water, but is almost discharged on rendering alkaline.

6-Methoxyindole-2-carboxydimethylacetalylmethylamide (Formula X),  
 11-Methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline (Formula XI), and 11-Methoxy-5-keto-4-methyl-4 : 5-dihydroindole-diazine(1 : 4) (Formula XII).

This series of substances, which represent the closing simultaneously of the carboline and indole-diazine rings (p. 1875), were obtained under the following conditions.

6-Methoxyindole-2-carboxylic acid was first converted into the acid chloride, and this combined with methylaminodimethylacetal in chloroform solution in the usual manner (compare Part V, p. 1626).

After distilling off the chloroform and adding water to the residue, 6-methoxyindole-2-carboxydimethylacetalylmethylamide separated at once in good yield and in an almost pure condition, since the melting point was  $127^{\circ}$ . It crystallised readily from light petroleum in colourless needles, the melting point rising to  $129^{\circ}$  (Found : C = 61.6; H = 6.9; N = 9.5.  $C_{15}H_{20}O_4N_2$  requires C = 61.6; H = 6.8; N = 9.6 per cent.).

*Action of Alcoholic Hydrogen Chloride.*—When the methylamide just described is added to a saturated alcoholic solution of hydrogen chloride at  $40^{\circ}$ , it dissolves and crystallisation usually takes place very slowly, but after twenty-four hours a yellow crust will have separated. This is filtered off, ground with very dilute ammonia, and the colourless precipitate collected by the aid of the pump, dried, and crystallised from alcohol. In this condition the substance melted indefinitely at about  $200^{\circ}$ , and examination under the microscope confirmed the suspicion that it was a mixture, since it was seen to consist of slender needles as well as of rhombic plates. On distillation with zinc dust, a sublimate was obtained which fluoresced distinctly blue in acid solution and also gave a purple coloration when warmed with Ehrlich's reagent (p. 1881), a behaviour which suggested the presence both of a carboline and of an indole-diazine. The separation of the two isomerides proved to be very difficult, but may be brought about by careful fractional crystallisation from alcohol repeated many times, the first crop consisting of the rhombic plates (m. p.  $245\text{--}246^{\circ}$ ). It was then observed that the rhombic plates are more sparingly soluble in acetone than the needles. In our later experiments, the crude mixture was therefore first extracted with a little warm acetone, and the small insoluble portion repeatedly fractionally crystallised from acetone and from alcohol until no needles could be detected under the microscope.

11-Methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline was thus obtained quite pure and melted at  $245\text{--}246^{\circ}$  (Found : C = 68.2; H = 5.1.  $C_{13}H_{12}O_2N_2$  requires C = 68.4; H = 5.2 per cent.).



This carboline yields a colourless hydrochloride on mixing with hydrochloric acid and gives scarcely any coloration with Ehrlich's reagent (p. 1881). The solution of the hydrochloride exhibits a distinct though very slight blue fluorescence, but when a trace of the base is distilled with zinc dust, the sublimate yields, on dissolving in very dilute hydrochloric acid, a strongly fluorescent solution. This is possibly due to the production of norhamine.

The mother-liquors from the purification of the carboline contain the isomeric indolediazine and this may be isolated in a pure condition in the form of yellow needles melting at  $205^{\circ}$  by repeated fractional crystallisation from alcohol (Found: C = 68.70; H = 5.24.  $C_{13}H_{12}O_2N_2$  requires C = 68.4; H = 5.2 per cent.).

11-Methoxy-5-keto-4-methyl-4 : 5-dihydroindolediazine(1 : 4) melts at  $205^{\circ}$  and gives a greenish-blue colour on gently warming with Ehrlich's reagent. This becomes fainter and greener on cooling and the effects can be produced alternately. On adding hydrochloric acid, a bright yellowish-brown colour is developed; this becomes brown and greenish-brown on heating, returning to reddish-brown on cooling. The addition of sodium nitrite subsequent to the treatment with Ehrlich's reagent produces a dull green; little change is observed on heating and the solution remains bluish-green on dilution with water.

The indolediazine gives with vanillin and hydrochloric acid in the cold a deep red colour which becomes very intense on heating. After dilution with water, the solution is red by transmitted and blue by reflected light. The colour is destroyed by the addition of alkali. Neutral or alkaline, but not acid, solutions have a distinct blue fluorescence, and the yellow solution in acetone or benzene exhibits a very strong green fluorescence. The hydrochloride differs from the colourless hydrochloride of the isomeric carboline in being yellow.

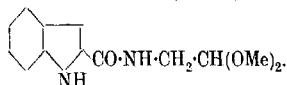
*N-Methyltetrahydronorharmine* (Formula XIV).

11-Methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline (1.3 grams) was dissolved in boiling *n*-butyl alcohol (20 c.c.), and sodium (2 grams) added. The solution became yellow and acquired a green fluorescence. In about two minutes ethyl alcohol was gradually added so as to keep the boiling solution clear and, when all the sodium had disappeared, dilute hydrochloric acid was added until an acid reaction to Congo was obtained. Steam was then passed into the brown-purple solution to remove the alcohols, and animal charcoal was added. The filtered solution was concentrated and, after cooling, rendered strongly alkaline by the addition of an excess of sodium hydroxide. This precipitated an ochre base which was

collected and dissolved as far as possible in much boiling benzene. The solution was treated with animal charcoal, filtered, and concentrated by distillation. An orange-yellow substance separated in a crystalline form and this was recrystallised from toluene and then twice from methyl alcohol. It was thus obtained in colourless, prismatic needles melting at  $182^{\circ}$ , and at the same temperature when intimately mixed with a specimen prepared by the method next to be described. A careful comparison disclosed no difference existing between the two substances. This material was not analysed, as very little was available, but was dissolved in acetone, cooled to  $-5^{\circ}$ , and finely powdered potassium permanganate added in minute amounts until after some hours no further oxidation occurred. More acetone was added and the solvent boiled and filtered. On concentration and adding water, a small, crystalline precipitate was thrown down, and the substance was collected and twice crystallised from alcohol. The oxidation product was thus obtained in colourless, prismatic needles melting at  $227^{\circ}$ , and at the same temperature when mixed with an authentic specimen of keto-*N*-methyltetrahydronorharmine prepared by the oxidation of harmaline methosulphate (Part III, p. 959). *N*-Methyltetrahydronorharmine is best prepared from keto-*N*-methyltetrahydronorharmine by reduction with sodium in butyl alcoholic solution and except that the operation was conducted on a somewhat larger scale (5 grams of the substance) the details of the process are precisely similar to those given above. Indeed the phenomena noticed at all stages were so alike in the two cases as to afford ground for the belief that the first action of the reducing agent on the carboline derivative is to convert it into ketomethyltetrahydronorharmine. One of the most striking coincidences was that in each case the paper used for the filtration following the steam distillation developed, on standing in the air, a purple colour at the apex and a beautiful blueish-green nearer the edges. The substance prepared by this method also melted at  $182^{\circ}$  (Found: C = 72.1; H = 7.3.  $C_{13}H_{16}ON_2$  requires C = 72.2; H = 7.4 per cent.). *N*-Methyltetrahydronorharmine is sparingly soluble in ether and very sparingly soluble in benzene. It dissolves readily in methyl or ethyl alcohol. When freshly prepared and purified, it is colourless, but on standing in the air it quickly becomes brownish-yellow as the result of oxidation. In this respect it differs from *N*-methyltetrahydroharmine, which is much more stable. In order to show the relation of the substance to norharmine, the base has been prepared from norharmine methosulphate (Part III, p. 951) by reduction with sodium and butyl alcohol. The yield in this case was unsatisfactory. The metho-

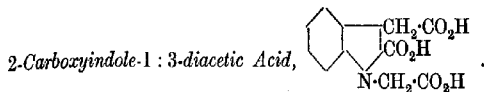
sulphate (1.8 grams) was dissolved in butyl alcohol (50 c.c.), and sodium (3 grams) added. The mixture was then boiled during twenty minutes by heating in an oil-bath, then diluted with alcohol, and the product isolated in the manner described above. The purification was difficult, but ultimately the substance was obtained pure and melted at  $182^{\circ}$ , and at the same temperature when mixed with a specimen made from ketomethyltetrahydronorharmine.

*Indole-2-carboxydimethylacetalyamide,*



With the object of obtaining further evidence concerning the direction of ring formation in the case of the action of hydrogen chloride on dimethylacetalyamides, this comparatively simple case was investigated. The preparation of the acid chloride of indole-2-carboxylic acid and its conversion into indole-2-carboxyacetalyamide are described in detail in Part V of this research (p. 1626), and in the present instance the same procedure was adopted except that aminodimethylacetal was employed in the place of aminoacetal and the condensation conducted in benzene instead of in chloroform solution, which appears to be an advantage. The acid chloride dissolves readily in boiling benzene and, after cooling and adding aminodimethylacetal (2 mols.), a viscid oil separates, which is not the case when chloroform is used as the solvent. The benzene was removed by distillation under reduced pressure, the residue mixed with water, and the solid product, obtained in a yield of 80 per cent. of theory dried in a vacuum desiccator. In this condition *indole-2-carboxydimethylacetalyamide* melts at  $129^{\circ}$  and is nearly pure, but after crystallisation from benzene, from which it separates as a matted mass of colourless needles, the melting point rises to  $130-131^{\circ}$  (Found: C = 63.1; H = 6.6.  $C_{13}H_{16}O_3N_2$  requires C = 62.9; H = 6.4 per cent.).

When this acetaly amide was warmed with alcoholic hydrogen chloride, it dissolved, and in a short time, yellow crystals of a hydrochloride commenced to separate. These were collected, ground with dilute ammonia, and the almost colourless base crystallised from alcohol, from which it separated in yellow needles melting at  $247^{\circ}$ . That this substance was 5-keto-4:5-dihydro-indole-diazine(1:4) was evident from the examination of its properties and was proved by admixture with the specimen of this substance which had previously been obtained (Part V, p. 1627), when the mixture melted at  $247^{\circ}$ .



This interesting acid, prepared during the course of the present investigation, is readily obtained under the following conditions.

Phenylhydrazinoacetic acid,  $\text{C}_6\text{H}_5\cdot\text{N}(\text{NH}_2)\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by the method recommended by Busch (*Ber.*, 1903, **36**, 3882) and dissolved in alcohol, is mixed with the quantity of  $\alpha$ -ketoglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , required to yield the hydrazone, and hydrogen chloride passed until the solution is saturated with the gas, the whole being cooled during the operation. On diluting the red solution with water, a crystalline precipitate comes down, which is collected, dried, and recrystallised from alcohol, from which it separates in slender, colourless needles (Found: C = 61.6; H = 6.0.  $\text{C}_{17}\text{H}_{15}\text{O}_5\text{N}$  requires C = 61.3; H = 5.7 per cent.). This diethyl ester of 2-carboxyindole-1:3-diacetic acid decomposes at  $200\text{--}202^\circ$ , dissolves in sodium carbonate in the cold, and, when heated, develops an odour resembling that of indole. With Ehrlich's reagent, it gives a bright red coloration which becomes blue on adding a drop of nitrite, and on dilution, purple and then green; the addition of hydrochloric acid brings back the purple colour.

2-Carboxyindole-1:3-diacetic acid is obtained from this ester by boiling with methyl-alcoholic potassium hydroxide; water is added, the methyl alcohol removed by evaporation, and the solution acidified, when colourless needles of this tribasic acid separate; these melt at  $261\text{--}263^\circ$  (Found: C = 56.2; H = 4.3.  $\text{C}_{13}\text{H}_{11}\text{O}_6\text{N}$  requires C = 56.3; H = 4.0 per cent.).

When phenylhydrazinoacetic acid is added to an alcoholic solution of pyruvic acid and hydrogen chloride passed, some ammonium chloride separates, and dilution with water precipitates an oil which does not solidify and is extracted with ether. After hydrolysis with alcoholic potassium hydroxide, dilution with water, and removal of the alcohol by evaporation, hydrochloric acid precipitates an acid which crystallises in long, flat needles and melts at  $232^\circ$ . This acid gives a red coloration on warming with Ehrlich's reagent and is evidently 2-carboxyindole-1-acetic acid. We propose to examine this acid and also 2-carboxyindole-1:3-diacetic acid in more detail.

*Py-N-Methyl-Ind-N-propylharmine Chloride (Formula XXIII).*

Pure methylharmine (4 grams) was dissolved in a hot mixture of nitrobenzene (15 c.c.) and toluene (15 c.c.), and propyl iodide

(5 c.c.) added. After boiling during ten minutes, the reaction, as indicated by the separation of methylpropylharmine iodide, appeared to be complete and, after cooling, the salt was collected and washed with ether. The iodide was converted to chloride by digestion on the steam-bath with water and an excess of precipitated silver chloride, and the crude salt thrown down from the filtered solution by the addition of sodium chloride and a little hydrochloric acid. The substance was then crystallised thrice from dilute hydrochloric acid and twice again from water. The crystals were collected and dried in the air, and this material lost 20.9 per cent. when dried at  $125^{\circ}$  (Found: in anhydrous material, C = 67.3; H = 7.9; Cl = 11.4.  $C_{17}H_{21}ON_2Cl \cdot 4.5H_2O$  requires  $H_2O = 21.0$  per cent.  $C_{17}H_{21}ON_2Cl$  requires C = 67.1; H = 6.9; Cl = 11.6 per cent.). Since the crystals lost some of their brilliancy on drying in the air, it is possible that they originally contained  $5H_2O$ . This substance is referred to below as (A).

*Py-N-Propyl-Ind-N-methylharmine Chloride (Formula XXII).*

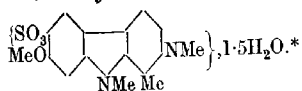
Harmine was quantitatively converted into its propiodide in the following manner. The base (4 grams) was heated with nitrobenzene (15 c.c.) until it dissolved, in a flask attached to a reflux condenser, and propyl iodide (10 c.c.) added. In a few seconds the propiodide crystallised in yellow prisms, and benzene (50 c.c.) was then added and the mixture boiled during an hour and a half. After cooling, the salt was collected and washed with benzene. The derivative crystallises very well from alcohol, in which it is sparingly soluble, in well-shaped, rectangular, prismatic needles which melt and decompose at  $240^{\circ}$ . Addition of sodium hydroxide to an alcoholic solution produces a yellow liquid which exhibits a striking green fluorescence.

This propiodide was converted to the corresponding chloride in the usual way by means of silver chloride, and the solution concentrated after filtration. On the addition of sodium chloride the chloride crystallised in pale yellow needles and was recrystallised from dilute brine. A hot aqueous solution was then rendered strongly alkaline by means of sodium hydroxide, and the oily yellow base extracted by warm toluene. This yellow extract, which exhibited green fluorescence, was rapidly separated and dried by warming with sticks of potassium hydroxide, and when thoroughly dry it was decanted, heated at  $100^{\circ}$ , and neutral methyl sulphate slowly added until the yellow colour had disappeared. A very pale yellow, crystalline substance separated almost immediately and this was collected and converted to chloride by crystallisation from dilute hydrochloric acid containing sodium chloride. Finally,

the substance was crystallised several times from water. Air-dried material lost 22.9 per cent. at 125° (Found: in anhydrous material, C = 67.4; H = 7.0; Cl = 11.8.  $C_{17}H_{21}ON_2Cl \cdot 5H_2O$  requires  $H_2O = 22.8$  per cent.  $C_{17}H_{21}ON_2Cl$  requires C = 67.1; H = 6.9; Cl = 11.6 per cent.). This substance is termed (B) in the comparison of properties of the two isomeric salts, which may now be made.

(A) melts at 130°, whereas (B) melts at 100°, and after resolidification (A) melts at 240° with decomposition whilst (B) still melts at about 100–110°. Both salts are hygroscopic when anhydrous. The isomerides are readily soluble in water, but (A) is much the more sparingly soluble of the two. The brilliant blue fluorescence of the aqueous solutions are identical. If to separate portions of an aqueous solution of (A) hydrochloric acid, nitric acid, sulphuric acid, or oxalic acid is added, an immediate crystalline precipitate of the corresponding salt is produced. These salts crystallise in small, colourless needles. With a solution of (B) of the same concentration, the salts are not immediately precipitated, but separate after some time in much larger slender needles. On the addition of potassium hydroxide to a solution of (A), there is produced a yellow liquid and a precipitate of yellow needles soluble in excess of water. With (B), however, the precipitate is a yellow oil also soluble in excess of water. A proof of the fact that (A) and (B) are different substances is afforded by the behaviour with sulphuric acid. Both give a yellow solution which exhibits bright green fluorescence and on warming becomes colourless and exhibits blue fluorescence. On diluting the solution of (A) in warm sulphuric acid, there is an immediate precipitate of a sulphonic acid. This substance is very sparingly soluble and crystallises in very small, colourless needles. (B), treated in the same way, never gives an immediate precipitate, but after some days the solution deposited crystals in this case also. These are short, slender, colourless needles similar to those obtained from (A), but exhibiting a greater tendency to form clusters. The sulphonic acid from (B), if used to inoculate subsequent preparations, produces an immediate crystallisation, but that from (A) has no such effect. Both (A) and (B) give very sparingly soluble mercurichlorides crystallising in pale yellow needles.

(A) gives a more flocculent, orange-yellow precipitate with potassium dichromate than does (B), whereas the buff ferrichloride from (B) is more flocculent than that from (A). Both salts give a green solution in concentrated nitric acid and a curious green oil when shaken with benzoyl chloride and aqueous potassium hydroxide.

*Dimethylharminesulphonic Acid,*

In Part III (p. 950), the very sparingly soluble methylharmine-sulphonic acid was described, and it was tentatively suggested that the substance might be an *N*-sulphonic acid derivative. In view of the fact that dimethylharmine chloride and the two methylpropylharmine chlorides yield similar derivatives, it must now be assumed that the sulphonic acid group enters the benzene nucleus. Dimethylharmine chloride (2 grams) was dissolved in sulphuric acid (10 c.c.). The yellow solution had a most brilliant green fluorescence, but the colour disappeared and the fluorescence changed to blue-violet on warming for a few seconds on the steam-bath. The mixture was added to excess of water, when an immediate precipitate of a very sparingly soluble substance was obtained. This was collected, washed with hot water, and dried at  $110^{\circ}$  (Found: C = 52.0; H = 5.7; S = 9.2.  $C_{15}H_{16}O_4N_2S \cdot 1.5H_2O$  requires C = 52.0; H = 5.5; S = 9.2 per cent.). This substance crystallises from a very large volume of water in slender, microscopic needles. It is insoluble in sodium carbonate and only dissolves in very dilute aqueous sodium hydroxide on heating

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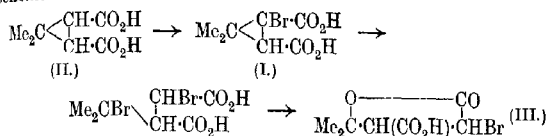
## CCXXVII.—*The Formation of Bromine Derivatives of Carbon Compounds without the Production of Hydrogen Bromide.*

By BIRAJ MOHAN GUPTA and JOCELYN FIELD THORPE.

MANY instances have doubtless occurred during organic chemical manipulation which have shown the disadvantages attaching to

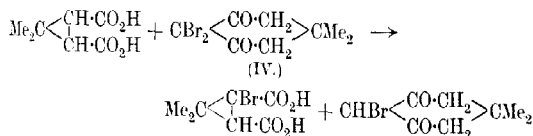
\* The manuscript of this communication was submitted before we had an opportunity to consult the suggestive paper of Pfeiffer (*Ber.*, 1922, **55**, [B], 1762) on the constitution of betaines and analogous substances such as the amino-acids and aromatic amino-sulphonic acids. The constitution which we now attribute to alkylharminesulphonic acids and exemplified in the symbol chosen to represent dimethylharminesulphonic acid is in complete harmony with Pfeiffer's views.

the formation of hydrogen bromide during the bromination of an organic substance by free bromine under the usual conditions, and have indicated the need for some method by which the production of the hydrogen haloid could be obviated. This need has been particularly evident during some of the work now being carried on in these laboratories, because it has often been found necessary to prepare bromo-derivatives (type I) of labile ring structures like caronic acid (type II), which, as is well known, readily undergo ring fission in the presence of hydrogen bromide, yielding derivatives of terebic acid (III) in accordance with the scheme



Consideration showed that a possible solution of the problem might be found in the use of compounds of the type of dibromodimethylhydroresorcinol (IV), which Norris and Thorpe (T., 1921, 119, 1205) have shown to possess a bromine atom which is in a state of such instability that it is replaced by hydrogen even through the agency of dilute caustic soda.

It seemed possible, therefore, that a reaction represented by the equation



might occur and that in this way the experimental difficulty mentioned above would be overcome. Before, however, trying the proposed reaction with costly and difficultly obtainable substances, we decided to ascertain its possibilities by the aid of commoner material, and the present communication describes our experiments in this connexion.

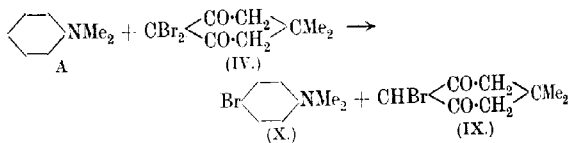
In the first place, it was desirable to determine which of the many substances containing unstable bromine were best suited for our purpose, and with this object in view we selected dimethylaniline as our compound to be brominated and the following dibromo-derivatives as our source of bromine: Ethyl dibromomalonate,  $\text{CBr}_2(\text{CO}_2\text{Et})_2$  (V), dibromomalondiethylamide,  $\text{CBr}_2(\text{CO} \cdot \text{NH} \cdot \text{Et})_2$  (VI), dibromocynoacetamide,  $\text{CN} \cdot \text{CBr}_2 \cdot \text{CO} \cdot \text{NH}_2$  (VII), dibromobarbituric



acid,  $\text{CBr}_2 \langle \begin{smallmatrix} \text{CO-NH} \\ \text{CO-NH} \end{smallmatrix} \rangle \text{CO}$  (VIII), and dibromodimethyldihydroresorcinol (IV).

It will be noticed that all these substances contain an unstable bromine atom in the sense that they all liberate iodine from potassium iodide, but it is certain that the degree of mobility or instability is markedly different in each case. We do not propose to discuss the question whether this difference in stability can be explained on the theory of relative polarities, or whether it is due, as has been suggested, to the tendency for the dibromo-derivative to acquire the hydrogen atom necessary to enable it to react in the enol form, but it is desirable to emphasise the fact, which is evident from the experiments described in this paper, that the greater the tendency for the compound containing the hydrogen atom to enolise the greater is its tendency to acquire that hydrogen atom and to do so by parting with one of the bromine atoms of its dibromo-derivative, or, in other words, the speed of the reaction between the brominator (A) and the acceptor (B) is determined by the tendency to enolise which is possessed by the mono-halogen compound (IX) formed in the reaction.

Thus ethyl dibromomalonate (V) and dibromomalon-diethylamide (VI), which would yield ethyl monobromomalonate and monobromomalon-diethylamide, respectively, do not react with dimethylaniline under ordinary experimental conditions, because the monobromo-derivatives possess little or no tendency to react in an enol form. On the other hand, dibromodimethyldihydroresorcinol (IV), which, when the necessary hydrogen atom is introduced, yields the strongly enolic substance monobromodimethyldihydroresorcinol (IX), reacts readily with dimethylaniline and in the course of a few minutes gives an almost quantitative yield of the brominated base (X),

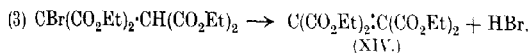
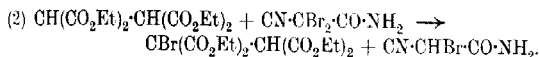
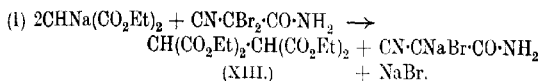


The method is therefore applicable for the purpose required, and it has been found that under suitable conditions it is possible, by its means, to brominate labile ring complexes without ring fission. It is especially useful because it is an easy matter to isolate the monobromo-derivative (IX), which can then be dibrominated and used again. The experiments in this connexion will form the subject of another communication.

The two other labile bromo-derivatives which were found to act as brominating agents, but to a less satisfactory degree than dibromodimethyldihydroresorcinol, were dibromobarbituric acid (VIII) and dibromocyanoacetamide (VII). Of the two, the barbituric acid derivative is the more satisfactory, giving a 75 per cent. yield of bromodimethylaniline. Dibromocyanoacetamide, under similar conditions, gives a 55 per cent. yield of the brominated base.

Dibromocyanoacetamide (VII) is a curious substance which was originally obtained by Hesse (*Amer. Chem. J.*, 1896, **18**, 725), but no experiments were carried out by him to determine the positions of the bromine atoms. This can be done quite easily, however, because the action of aniline leads to the formation of the compound  $\text{NHPh}\cdot\text{C}(\text{NPh})\cdot\text{CO}\cdot\text{NH}_2$  (XI), from which phenyloxamide  $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$  (XII) can be prepared by hydrolysis.

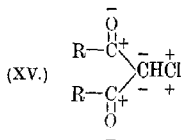
The action of ethyl sodiomalonate on the dibromo-compound (VII) is typical, ethyl ethanetetracarboxylate (XIII) and ethyl ethylenetetracarboxylate (XIV) being produced in approximately equal amounts. It is evident, therefore, that dibromocyanoacetamide acts as free bromine, and that the course of the reactions is represented by the equations



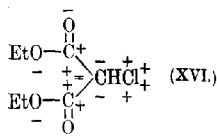
It is doubtless desirable to carry out the brominating reactions, of which those described in this paper are types, in solvents, such as carbon tetrachloride, from which the brominator cannot acquire the hydrogen atom it desires. Actually, in the present experiments, in which the reactions proceeded easily and rapidly, this precaution was not found to be necessary, and solvents such as alcohol and benzene were used without detriment to the yield of brominated base.

A paper has just appeared by Macbeth (this vol., p. 1118) in which the "tautomeric hypothesis" of Thole and Thorpe (*T.*, 1911, **99**, 2183) is criticised. Macbeth prefers the "polarity hypothesis," because, for example, a substance such as ethyl monochloromalonate (XV) reacts with hydrazine to form ethyl malonate and free nitrogen, whereas monochloroacetylacetone (XVI) and, incidentally, its

dichloro-derivative, do not behave in this manner. The polarity explanation of this is as follows:

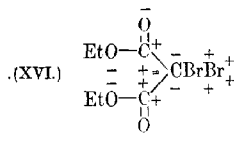


(Halogen not reactive.)

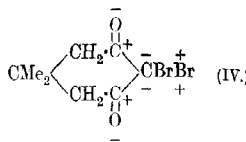


(Halogen reactive.)

and therefore it follows that:



(Halogen more reactive.)



(Halogen less reactive.)

which is totally contrary to the actual experimental facts as described in this paper.

## EXPERIMENTAL.

### A.—Dibromocyanoacetamide (VII).

The method of preparation adopted was similar to that employed by Hesse (*loc. cit.*), but the yield was increased to 90 per cent. of the theory by the following modification of his process. Cyanoacetamide (42 grams; 1 mol.) was dissolved in 350 c.c. of cold water and the solution treated with 160 grams of bromine, a small quantity being added at a time and the mixture being kept cool. Addition of sodium acetate in quantity sufficient to react with the hydrobromic acid formed in the reaction, increases the yield and prevents the formation of lachrymatory polybromo-compounds. The precipitate obtained was quickly filtered, freed from traces of adhering hydrobromic acid by washing, and dried. A pure specimen, crystallised from benzene, melted at 126° (Found: Br = 65.97. Calc., Br = 66.1 per cent.). All attempts to prepare monobromocyanoacetamide by direct bromination were fruitless, and it was not until later (see p. 1902) that this substance was obtained in another way.

*Action of Sodium Hydroxide. Formation of Tribromoacetamide,  $\text{CBr}_3\text{CO}\cdot\text{NH}_2$ .*—Dibromocyanoacetamide dissolves readily in dilute caustic soda and, in a short time, a heavy oil is precipitated which contains bromoform and carbon tetrabromide. Deep-seated decomposition of this kind is, however, prevented if carbamide is present.

One gram of dibromocyanoacetamide was mixed with 4 grams of carbamide dissolved in water, and a 10 per cent. solution of caustic soda added drop by drop until complete solution had been effected. The solution, which became reddish-brown, was then extracted with ether, and the crystalline residue, left after evaporating the ether, recrystallised from dilute alcohol. The pure tribromoacetamide melted at  $120-121^{\circ}$  (Found: C = 8.16; H = 0.70; Br = 80.8.  $C_2H_2OBr_3$  requires C = 8.1; H = 0.7; Br = 81.0 per cent.).

*Action of Ethyl Sodiomalonate.*—Dibromocyanoacetamide (24 grams) was dissolved in 75 c.c. of ethyl alcohol and the cooled solution added gradually to a suspension of ethyl sodiomalonate (0.2 mol.) in 65 c.c. of ethyl alcohol. After the solution had stood on ice over-night, it was heated on the water-bath for one hour and then diluted with water. The oil which was extracted by ether and became partly solid on standing was distilled under 30 mm. pressure, the fraction boiling at  $110-130^{\circ}$ , which became completely solid on cooling, being collected. The crystals, which melted at  $50^{\circ}$ , were found to consist of two substances which could be separated by repeated crystallisation from a mixture of alcohol and light petroleum. One of these melted at  $56^{\circ}$  and was identified by means of its properties and by its hydrolysis to fumaric acid as ethyl ethylenetetracarboxylate (XIV); the other, which melted at  $76^{\circ}$ , was found to be ethyl ethanetetracarboxylate (XIII).

*Action of Aniline. Formation of Diphenylamidinoexamide (XI).*—When a mixture of 24 grams of dibromocyanoacetamide and 37 grams of aniline dissolved in 20 c.c. of absolute alcohol is left at the ordinary temperature, it gradually becomes warm and in about half an hour a vigorous reaction takes place, the whole mass becoming solid. A considerable portion of this proved to be aniline hydrobromide, which could be removed by the action of hot water, leaving an insoluble residue which, when crystallised from alcohol, formed lustrous, pale yellow laminae, melting at  $155^{\circ}$  (Found: C = 69.90, 70.06; H = 5.62, 5.54; N = 17.68, 18.09. Calc., C = 70.2; H = 5.5; N = 17.6 per cent.). This substance is evidently identical with that prepared by Schultz, Rohde, and Herzog (*J. pr. Chem.*, 1906, [ii], 74, 74) from hydrocyanocarbodiphenylimide.

*Phenyloxamide.*—The proof of structure of the last-named substance was provided by its hydrolysis to phenyloxamide. Diphenylamidinoexamide dissolves readily in dilute hydrochloric acid and, if the solution is warmed for a few minutes, phenyloxamide separates on cooling. It melts at  $225^{\circ}$  and sublimes very easily (Found: C = 57.82; H = 4.86; N = 17.68. Calc., C = 58.5; H = 4.9; N = 17.1 per cent.).

*Action of Dimethylaniline. Interchange of Hydrogen and Bromine.*

—Six grams of dibromocyanoacetamide were dissolved in 120 c.c. of dry benzene and the warm solution was treated with 3 grams of dimethylaniline. The colour of the solution gradually turned greenish-blue and, on keeping the mixture at 80°, a dark brown liquid slowly separated. The heating was continued for four to five hours. After cooling, the liquid was separated from the solid which had formed, and the solvent evaporated. The solid residue proved to be *p*-bromodimethylaniline, melting at 58°. *Monobromocyanoacetamide*,  $\text{CHBr}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ , can be isolated from the product insoluble in benzene. It forms colourless crystals from alcohol and melts at 120–121° (Found: C = 22.16; H = 1.96; Br = 49.05.  $\text{C}_3\text{H}_3\text{ON}_2\text{Br}$  requires C = 22.1; H = 1.9; Br = 49.04 per cent.).

The amounts of monobromocyanoacetamide and *p*-bromodimethylaniline actually isolated represented 55 per cent. of the theoretical yields.

*B.—Ethyl Dibromomalonate (V).*

Ethyl dibromomalonate was prepared by the action of bromine on ethyl malonate in the presence of sunlight according to the method described by Conrad and Bruckner (*Ber.*, 1891, 24, 2993). A pure specimen was obtained by redistillation, and the fraction distilling between 148–155°/25 mm. was employed in these experiments.

*Action of Dimethylaniline.*—A mixture of 3.1 grams of ethyl dibromomalonate, 1.2 grams of dimethylaniline, and 5 c.c. of dry benzene was heated on the steam-bath for five hours. After boiling off the solvent, the residual liquid was treated with dilute hydrochloric acid. The acid extract was then made alkaline and extracted with ether, the ether on evaporation leaving a residue which consisted mainly of the initial materials. No trace of *p*-bromodimethylaniline could be detected.

*C.—Dibromomalondiethylamide (VI).*

This substance was obtained by the action of bromine on malondiethylamide, which was prepared by the interaction of ethylamine and ethyl malonate. The bromination was effected in two stages in accordance with the method described by Backes, West, and Whiteley (*T.*, 1921, 119, 363). The specimen used in these experiments had been extracted with dry ether and recrystallised from a mixture of alcohol and light petroleum. It melted at 78°.

*Action of Dimethylaniline.*—3.2 Grams of dibromomalondiethylamide were dissolved in 50 c.c. of dry benzene and treated with 1.2 grams of dimethylaniline, the mixture being boiled for two hours. After removing the solvent, the residue was treated with dilute

hydrochloric acid and filtered from the insoluble material, which was found to be unchanged dibromomalondiethylamide, 2.9 grams being recovered in this way. The unchanged dimethylaniline was isolated from the filtrate by rendering it alkaline. The quantity obtained was practically the same as the amount originally employed. No trace of *p*-bromodimethylaniline could be detected.

#### D.—Dibromobarbituric Acid (VIII).

Crystallised barbituric acid (1 mol.) was dissolved in boiling water and the solution treated gradually with bromine (2 mols.), which was rapidly absorbed. The material used in these experiments, which melted at 235°, was isolated by extracting the cooled solution with ether and recrystallising the ether extract.

*Action of Dimethylaniline.*—Owing to the insolubility of dibromobarbituric acid in benzene and in carbon tetrachloride, the solvent used in this case was absolute alcohol. Dibromobarbituric acid (2.8 grams) was dissolved in warm alcohol and the solution treated with 1.2 grams of dimethylaniline. A vigorous reaction, with the evolution of heat, took place at once, but in order to ensure that it was carried to completion, the mixture was heated for fifteen minutes on the water-bath. After removing the solvent, the residue was extracted with light petroleum (b. p. 50–60°) and in this way an amount of *p*-bromodimethylaniline corresponding with 75 per cent. of that theoretically possible was isolated.

#### E.—Dibromodimethyldihydroresorcinol (IV).

Dimethyldihydroresorcinol, prepared by the method of Norris and Thorpe (T., 1921, **119**, 1205; compare also Vorländer, *Annalen*, 1897, **294**, 253), was dibrominated in chloroform solution by the method described by Vorländer and Kohlmann (*Annalen*, 1902, **322**, 257). The product used had been recrystallised from dilute methyl alcohol. It melted at 144°.

*Action of Dimethylaniline.*—A mixture of 3 grams of dibromodimethyldihydroresorcinol and 1.2 grams of dimethylaniline was treated with 15 c.c. of dry benzene, and the solution heated for fifteen minutes on the water-bath. After evaporating the benzene, the dry residue was treated with dilute hydrochloric acid and filtered. The filtrate yielded, on being made alkaline, a quantity of *p*-bromodimethylaniline which represented more than 90 per cent. of that theoretically possible. The residue insoluble in dilute hydrochloric acid was, after purification, identified as monobromodimethyldihydroresorcinol (IX), melting at 175°. It was evident, therefore, that the reaction had proceeded practically quantitatively, the percentage yields of the two products being the same.

An experiment carried out with dimethylaniline and monobromodimethyldihydroresorcinol (IX) showed that no reaction occurred between these two substances.

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CCXXVIII.—*The Reactivity of Alkyl Iodides with Sodium Benzyloxide and the Effect of Temperature on such Reactions.*

By PERCY CHARLES HAYWOOD.

THE interaction of the alkyl iodides and a variety of compounds has been studied by numerous investigators, but only Slaton (T., 1904, **85**, 1286), Preston and Jones (T., 1912, **101**, 1930), and Segaller (T., 1914, **105**, 106) appear to have studied the effect of temperature on the relative reactivities. Various methods have been adopted to attain this end, and in general it has been observed that methyl iodide is several times more reactive than ethyl iodide, whilst the other members of the series show a comparable decreasing reactivity with increase of molecular weight. No definite relationship was established, however, between these two specific properties.

Wislicenus (*Annalen*, 1882, **212**, 239) measured the velocity of the reaction between ethyl sodioacetoacetate and the alkyl haloids in ethyl-alcoholic solution. Wildermann and Aisinmann (*Z. physikal. Chem.*, 1891, **8**, 661) investigated the rate at which hydrogen haloid was split off from halogen derivatives of the fatty hydrocarbons by alcoholic potash. At 35.5°, they found that ethyl iodide was destroyed three times as quickly as propyl iodide and that isoamyl iodide, isopropyl iodide, and *sec*-hexyl iodide decreased in activity in the order given. This type of reaction was later studied by Brussoff. Hecht, Conrad, and Bruckner (*ibid.*, 1889, **4**, 272) studied the reaction in alcoholic solution between sodium ethoxide and the alkyl iodides at 30°. The reaction in this case too was found to be bimolecular, but their results did not agree in detail with those of Wislicenus. The bimolecular reaction between the alkyl haloids and triethylamine in acetone at 100° was investigated by Menschutkin (*ibid.*, 1890, **8**, 589), who found an anomaly in the behaviour of the methyl haloid. Conrad and Bruckner, in continuation of their investigation on the velocity of ether formation (*ibid.*, 1891, **7**, 274), measured the velocity coefficients with a reaction mixture of alkyl

Table showing the Relative Reactivity of Various Alkyl Iodides as Determined by Numerous Investigators.

Iodide.	Wislicenus.	Hecht and Conrad.	Men. schutkin.	Wildermann.	Brusoff.	Burke and Donnan.	Slator.	Preston and Jones.		Cox.	
								(1)	(2)	(1)	(2)
Methyl .....	934.6	1268	1129			41.5	1800	1500	7785	572.5	359 398.7
Ethyl .....	100	100	100	100	100	100	100	100	100	100	100
n-Propyl .....	23.8	35	14.2	31.5	135	46.8		31.3	23.8	38.6	52.4 46.5
iso-Propyl .....	8.2	18.9	1.4	22	171	103				35.67	
n-Butyl .....			13.7		60	30.8				37.2	
iso-Butyl .....	3.8		1.4		171	6.5				14.5	
iso-Amyl .....				12.6 47		26.7				19.2	
sec-Hexyl .....				75.6 101						33	
n-Heptyl .....		21.3	13.7							33.9	
n-Octyl .....		20.5	10.7							32.7	
sec-Octyl .....										33.6	
Hexadecyl .....										32.2	

Preston and Jones (1) Reaction between alkyl iodide and dimethylaniline. (2) Reaction between alkyl iodide and triisooxylaniline.

Cox (1) Reaction with sodium  $\alpha$ -naphthoxide in ethyl alcohol at dilution  $v = 10$ .(2) Reaction with sodium  $\beta$ -naphthoxide in ethyl alcohol at dilution  $v = 10$ .



iodide, sodium ethoxide, and phenol. The rate of evolution of gaseous olefine by the interaction of alkyl haloids and 2*N*-potassium hydroxide in 96 per cent. alcohol, at 78° was determined by Brussoff (*ibid.*, 1900, **34**, 129). His reaction mixture was not initially at 78° and thus there must be an appreciable error in his results. Burke and Donnan (T., 1904, **85**, 585) carried out an investigation of the bimolecular reaction between the alkyl iodides and silver nitrate. In this case, silver iodide being precipitated, the introduction of this new phase may possibly have influenced the velocity of the reaction. There is also a possibility of complex silver salts being formed. The velocities of the reaction of sodium thiosulphate with methyl iodide and also with ethyl iodide at 25° were studied by Slator (*loc. cit.*). The velocity of the reaction with methyl iodide was eighteen times as great as that with ethyl iodide, and the ratio  $k_{\theta+10^{\circ}}/k_{\theta}$  was equal to 3.0 and 3.4 in the cases of methyl and ethyl iodides, respectively. Following on the work of Menschutkin, Preston and Jones (*loc. cit.*) studied the action of alcoholic solutions of the alkyl haloids on dimethylaniline and triisobutylamine at 25° and 40°. Their results also show an anomaly in the behaviour of methyl iodide. Furthermore, in each case, the ratio of the velocity of reaction of each iodide at 40° to the velocity at 25° was approximately constant. Cox (T., 1918, **113**, 666) studied the reaction of sodium  $\alpha$ -naphthoxide and sodium  $\beta$ -naphthoxide with some normal iodides in decinormal alcoholic solution at 40°. The only extensive investigations of the influence of temperature on the reactivity of the alkyl iodides are due to Segaller (*loc. cit.*). He determined the velocity coefficient of the reaction between aliphatic iodides and sodium phenoxide in alcoholic solution, and found the data obtained were well expressed by Arrhenius's equation (*Z. physikal. Chem.*, 1887, **4**, 226), and that the relative reactivity was approximately independent of temperature, with the exception of *n*-heptyl and hexadecyl iodides at the highest temperatures.

The numerical results obtained by the various investigators are summarised in the preceding table.

In previous determinations of the relative reactivity of certain aliphatic iodides, the general method has been to study the reaction between the iodides and the sodium derivative of either an aliphatic or an aromatic alcohol, for example, sodium ethoxide or sodium phenoxide. It was considered an advantage to study the effect on some aliphatic iodides of sodium benzyloxide, which, although aromatic, has properties appertaining rather to the aliphatic series than to the homocyclic. By such means it was hoped that a definite relationship between the reactivity and the molecular weight of an iodide would be obtained.

The rate of reaction was measured by titrating the alkalinity of the mixture at definite intervals of time. Fifty c.c. of *N*/5-sodium benzyloxide were intimately mixed with 50 c.c. of *N*/5-solution of the iodide, the solvent in each case being pure ethyl alcohol. Ten c.c. of this mixture were transferred as rapidly as possible to each of nine Jena-glass test-tubes, which were immediately closed by well-fitting rubber stoppers. These tubes were placed in a brass rack, lowered into the thermostat, and allowed fifteen minutes in which to attain the correct temperature. At this juncture a tube was withdrawn and the mixture poured into a titration flask containing almost the correct amount of acid for neutralisation (determined by previous experiment). The tube was carefully washed and the diluted mixture made up to 200 c.c. with cold water; acid was then added until neutralisation was complete using phenolphthalein as indicator. After dilution, alcohol was present only to an extent of 5 per cent. and the phenolphthalein was thus capable of giving an accurate end-point, the maximum error of titration being  $\pm 0.13$  per cent. After definite time intervals, other tubes were withdrawn and their alkalinity determined. From these values the velocity of reaction was calculated.

The acid used was standard hydrochloric acid, obtained from "constant boiling" acid. The thermostat employed was of the general type. The surface of the water was covered with a layer of lubricating oil of low density, and a special electrical device was employed for the maintenance of a constant temperature, with very satisfactory results. A detailed description of this apparatus will be published in a later paper. In experiments extending over a period of nine hours, no alteration in temperature could be detected, whilst for those of a longer duration, in which comparatively large changes in atmospheric temperature would be experienced, the variation was in the region of  $0.01^\circ$ . The majority of the experiments at  $60^\circ$ , however, were carried out in a thermostat provided with an adapted Ostwald toluene thermo-regulator, with temperature variation of  $\pm 0.01^\circ$ .

Since we have the reaction



one would expect it to be of the second order; experiments show that such is the case.

The results were calculated by the usual formula and expressed as  $k$  in terms of gram-molecules per litre.

$$k = \frac{y}{C_0 a} \left[ \frac{1}{t} \cdot \frac{x}{a-x} \right] = \frac{y}{C_0 a} \cdot k',$$

where  $y$  = c.c. of acid required to neutralise the amount of sodium

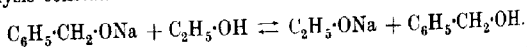
benzyloxyde in a known volume of the mixture before the commencement of the experiment,  $a$  = c.c. of acid required to neutralise the same volume of the mixture at the zero point taken,  $(a - x)$  = c.c. required to neutralise an equal volume at a time  $t$  minutes from this zero, and  $C_0$  = concentration of reacting substances at the theoretical zero.

Since in the preparation of sodium benzyloxyde there was a possibility of a slight excess of the alcohol, it was considered advisable to study the effect of the presence of excess of this alcohol in the reaction mixture. In absence of excess of benzyl alcohol, the velocity of reaction between sodium benzyloxyde and ethyl iodide of  $N/10$ -concentration in ethyl alcohol at  $40^\circ$  was found to be  $k = 0.04556$ , whilst in the presence of 5 per cent. excess of benzyl alcohol  $k = 0.04422$ . Thus, for a 5 per cent. excess of benzyl alcohol, we have a decrease of 3.5 per cent. in the velocity coefficient. Similar results were obtained by Cox (*loc. cit.*) and by Robertson and Acree (T., 1913, 49, 474) in the reaction between  $N/2$ -sodium phenoxide and  $N/2$ -methyl iodide.

The effect of a small percentage of water was also investigated. The velocity coefficient of the reaction at  $40^\circ$  between ethyl alcohol and sodium benzyloxyde of equivalent  $N/10$ -molecular concentration is 0.04556; whilst in the presence of 1 per cent. of water by weight, we have a velocity constant,  $k = 0.04588$ . This gives an increase of 0.5 per cent. approximately, and thus a trace of water as impurity in the solvent will not cause a large error. In this connexion, it must be mentioned that Cox (T., 1920, 117, 502) observed an increase of 3 per cent. in the velocity coefficient when 95 per cent. alcohol was used as the solvent in the place of 100 per cent. alcohol.

The flasks, pipettes, and burettes used were standard, and the same were used throughout the series of experiments. As an additional precaution, the solution of sodium benzyloxyde prepared by solution of a known weight was checked by titration with standard hydrochloric acid obtained from "constant boiling" acid. Precautions were also taken to exclude carbon dioxide and moisture.

On dissolving sodium benzyloxyde in ethyl alcohol, one would expect alcoholysis to take place to a certain extent until the alcoholysis constant was satisfied:

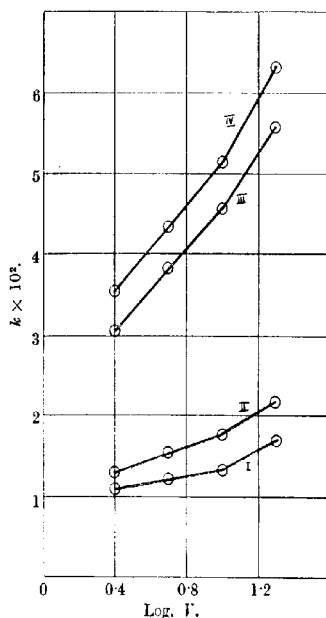


Similarly, a mixture of sodium ethoxide and benzyl alcohol in ethyl alcohol solution would result in the formation of sodium benzyloxyde, the alcoholysis constant being the same under these

conditions. That such is the case is shown by the following examples.

FIG. 1.

*Relationship between the velocity coefficient and the logarithm of the dilution.*



I Ethyl iodide at 30°. II n-Propyl iodide at 40°.  
 III " " " 40°. IV " " " 50°.

A reaction mixture of  $N/10$ -ethyl iodide and  $N/10$ -sodium benzyloxide at 40° has for its velocity coefficient  $k = 0.04556$ . Using a mixture of sodium ethoxide and benzyl alcohol in place of the sodium benzyloxide, a coefficient,  $k = 0.04560$ , was obtained.

Again with  $n$ -propyl iodide. A reaction mixture consisting of  $N/10$ - $n$ -propyl iodide and  $N/10$ -sodium benzyloxide has the velocity coefficient of interaction at 50°,  $k = 0.05119$ . When the sodium benzyloxide was replaced by equal molecular quantities of sodium ethoxide and benzyl alcohol, the determined velocity coefficient was  $k = 0.05070$ . This equivalency of sodium benzyloxide in ethyl alcohol solution and a solution of sodium ethoxide with benzyl alcohol of corresponding concentration in ethyl alcohol

has been used in the determination of the velocity of reaction in preliminary experiments.

The initial concentration is of considerable importance, for experiment shows that to obtain comparable results the same initial concentration should be used for each substance.

An empirical equation was proposed by Hecht, Conrad, and Bruckner (*Z. physikal. Chem.*, 1890, **5**, 289),

$$k_{r_1} - k_{r_2} = a \log v_1/v_2,$$

where  $k_{r_1}$  and  $k_{r_2}$  are the velocity coefficients of the reaction under consideration in terms of gram-molecules per litre at dilutions  $v_1$  and  $v_2$  respectively. This expression was later placed on a scientific basis by Schroeder and Acree (*T.*, 1914, **105**, 2582).

The velocity coefficients for ethyl and *n*-propyl iodides at dilutions 2.5, 5, 10, and 20, each at two temperatures, have been determined and the results are shown graphically in Fig. 1.

(A) *Ethyl Iodide.*

Temp.	$k_{2.5}$ .	$k_{10}$ .	$a$ .	$k_5$ (calc.).	$k_5$ (obs.).	$k_{20}$ (calc.).	$k_{20}$ (obs.).
30°	0.01093	0.01423	0.00548	0.01258	0.01247	0.01588	0.01692
40°	0.03057	0.04556	0.0249	0.03801	0.03823	0.05306	0.05569

(B) *n-Propyl Iodide.*

Temp.	$k_{2.5}$ .	$k_{10}$ .	$a$ .	$k_5$ (calc.).	$k_5$ (obs.).	$k_{20}$ (calc.).	$k_{20}$ (obs.).
40°	0.01292	0.01758	0.00774	0.01525	0.01549	0.01991	0.02174
50°	0.03533	0.05124	0.0264	0.04490	0.04341	0.05756	0.06306

The values of a  $k_5$  (calc.) and  $k_{20}$  (calc.) are obtained from  $k_{2.5}$  and  $k_{10}$ .

From these values of the velocity coefficients it can be seen that the equation does not hold with accuracy at a dilution of  $v = 20$ . Cox (*T.*, 1920, **117**, 505), in his investigations on the reaction between the naphthoxides and alkyl iodides, noticed that in the case of methyl iodide in ethyl-alcoholic solution there was a distinct change at a dilution of  $v = 8$ . Thus, in order to obtain comparative results of the reactivity of the iodides by the method under consideration, the velocity of reaction must be studied at the same dilution (compare also Segaller, *loc. cit.*).

Lewis has deduced on the basis of the quantum theory an expression for the variation of velocity coefficient with temperature (*T.*, 1916, **109**, 807). This expression differs from that of Arrhenius by a correction term applied to the coefficient. In the case of ethyl alcohol, the temperature coefficient of refractivity is 0.0004 (Ketteler, *Ann. Phys. Chem.*, 1888, [iii], **33**, 508), causing a variation of a constant, of the order determined experimentally, of

approximately 0.15 per cent. The expression deduced by Robertson and Acree (*J. Amer. Chem. Soc.*, 1913, **49**, 474) shows that alcoholysis has no effect on the constancy of this relationship. The results obtained are compatible with the radiation hypothesis.

*Preparation and Purification of the Chemical Used.*—Benzyl alcohol, containing slight impurities of benzyl chloride and benzaldehyde, was heated under reflux with a strong solution of caustic potash. The product after separation from the alkali was fractionated to free it from as much water as possible, and finally dried by heating under reflux with, and then distilling from, freshly prepared calcium turnings. The alcohol obtained after careful refractionation had b. p. 206.2°.

The alkalinity, as compared with the estimation as sulphate, of the sodium used in the preparation of the oxide gave a purity of 99.98 per cent.

Sodium benzyloxide was best prepared by the following methods: (I) Sodium was dissolved in an excess of benzyl alcohol in a current of pure dry hydrogen (obtained by electrolysis of dilute sulphuric acid), the liquid being warmed. The excess of benzyl alcohol was distilled off at as low a pressure as possible, because charring readily took place on heating too strongly. Finally, the substance was gently heated in a current of hydrogen. Alternative methods for the removal of the last trace of benzyl alcohol were used, such as extraction with small quantities of xylene, light petroleum, etc. The first method was found, however, to be the easiest from the practical point of view.

(II) On addition of the correct quantity of sodium to a solution of benzyl alcohol in xylene, previously purified by distillation over that metal, solution slowly took place. After removal of the xylene by distillation under diminished pressure, the product was finally purified from xylene by heating at 100° in a stream of hydrogen. When obtained pure, the compound consisted of white flakes which were only slightly hygroscopic and could be kept for some considerable period in a vacuum desiccator over paraffin (Found: Na = 17.67, 17.71. Calc., Na = 17.69 per cent.).

Owing to the great difficulty of purchasing pure iodides, nearly all such used in this research were synthesised. From purified methyl and ethyl alcohols the corresponding iodides were obtained by the standard method, by addition of iodine to red phosphorus and the alcohol, using a 10 per cent. excess of iodine (methyl iodide, b. p. 42.5°, ethyl iodide, b. p. 72.4°). The yield was considerably increased by treating the reaction product, after keeping for twenty-four hours, with a small quantity of water and heating under reflux.

n-Propyl alcohol was obtained from propyl acetate and con-

verted into the corresponding iodide (b. p. 102.0°) by the usual process.

*iso*Propyl iodide, prepared from glycerol, was finally obtained pure only by careful fractionation in almost complete absence of light (b. p. 39.5°).

*n*-Butyl alcohol was isolated from fermentation butyl alcohol. Careful fractionation of a sample gave 13 per cent. and 49 per cent. of distillate boiling at 115–116° and 116–117° respectively. These fractions were mixed, dehydrated over potassium carbonate, lime, and finally calcium turnings, and again distilled. After two fractionations, the alcohol, b. p. 116–116.5°/756 mm., was accepted.

*n*-Butyl iodide, b. p. 129.6°, was prepared by the standard method.

*iso*Butyl iodide, b. p. 120.0°, was synthesised from *isobutyl* alcohol.

*sec*-Hexyl iodide was obtained by destructive distillation of mannitol with hydriodic acid in the presence of carbon dioxide. The best yield was obtained by dissolving the mannitol in the requisite quantity of water, mixing with iodine, and finally adding yellow phosphorus until the solution was colourless. This mixture was heated under reflux for twenty minutes and the *sec*-hexyl iodide distilled off under slightly diminished pressure in the presence of carbon dioxide. Careful fractionation under diminished pressure (<50 mm.) gave the desired product (b. p. 85.0°/43 mm.). A specimen of Kahlbaum's *sec*-hexyl iodide was obtained at a later date, and after purification its reactivity was found to agree with that of the prepared iodide.

*n*-Heptyl iodide (b. p. 203.5°) was synthesised from *n*-heptyl alcohol. Both *n*- and *sec*-octyl iodides were Kahlbaum's chemicals.

Hexadecyl iodide, m. p. 22°, was prepared from hexadecyl alcohol by the general method of synthesis and was purified by preparing a saturated solution in alcohol at 20° and immersing in a freezing mixture. A second specimen was obtained by purification of a small quantity of Kahlbaum's iodide. The rates of reaction of both specimens showed good agreement.

The iodides were purified by careful fractionation in an atmosphere of carbon dioxide, they having been previously treated with dilute alkali solution to remove iodine, washed free from alkali, and dried over calcium chloride. After a final distillation over freshly ignited silver, under such a pressure that decomposition did not take place, the iodides were kept in blackened bottles over small quantities of ignited silver and calcium chloride.

The solvent, ethyl alcohol, used was commercial absolute alcohol which had been boiled under reflux and distilled over fresh quick lime; the last traces of water were removed by heating under reflux and distilling over freshly prepared calcium turnings. The

distillate was collected in a receiver provided with a drying-tube, and transferred to well-stoppered, green-glass bottles.

### Results.

Only one complete experiment is given with each iodide, the other results being summarised for economy of space. The experiments selected are given at different temperatures in order to indicate the trustworthiness of the results at the lower and higher temperatures. In this series of experiments each mixture consisted of 5 c.c. of *N*/5-sodium benzyloxiide and 5 c.c. of *N*/5-solution of the iodide under investigation. In all cases the acid was *N*/40-hydrochloric acid and  $y = 40$ .

#### Methyl iodide.

Temp. 0°. Zero = 38.65 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
120	37.00	1.65	3716
330	34.40	4.25	3744
615	31.45	7.20	3720
900	28.95	9.70	3723
1204	26.50	12.15	3722
1530	24.60	14.05	3715
1935	22.55	16.10	3689
2415	20.45	18.40	3685

$$k' \text{ (mean)} = 0.0003714$$

$$k = k' \times 400/38.65 = 0.003844$$

#### Ethyl iodide.

Temp. 30°. Zero = 39.00 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
15	38.20	0.80	1396
60	36.00	3.00	1389
115	33.60	5.40	1397
180	31.20	7.80	1389
255	28.90	10.10	1375
360	26.06	12.94	1379
425	24.70	14.30	1367
465	23.70	15.30	1389

$$k' \text{ (mean)} = 0.001391$$

$$k = k' \times 400/39.00 = 0.01426$$

#### *n*-Propyl iodide.

Temp. 60°. Zero = 33.90 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
4	32.35	1.65	1278*
8	30.85	3.05	1236
12	29.60	4.30	1211
17	28.00	5.90	1240
24	26.20	7.70	1225
33	24.20	9.70	1214
45	21.85	12.05	1226
60	19.40	14.50	1246

$$k' \text{ (mean)} = 0.01228$$

$$k = k' \times 400/33.90 = 0.1440$$

#### isoPropyl iodide.

Temp. 30°. Zero = 39.45 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
180	37.30	2.15	3202
380	35.05	4.40	3304
620	32.75	6.70	3300
860	30.80	8.65	3265
1160	28.65	10.80	3248
1520	26.30	13.15	3290
1960	24.00	15.45	3284
2260	22.75	16.70	3248

$$k' \text{ (mean)} = 0.0003268$$

$$k = k' \times 400/39.45 = 0.003314$$

#### *n*-Butyl iodide.

Temp. 40°. Zero = 38.95 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
45	36.80	2.15	1298
105	34.60	4.35	1195*
200	31.10	7.85	1262
280	28.72	10.23	1272
370	26.50	12.45	1270
480	24.40	14.55	1243
630	21.46	17.49	1293

$$k' \text{ (mean)} = 0.001273$$

$$k = k' \times 400/38.95 = 0.01307$$

#### isoButyl iodide.

Temp. 60°. Zero = 34.30 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
6	32.20	2.10	1086
13	30.00	4.30	1103
20	28.20	6.10	1081
30	25.70	8.60	1115
40	23.85	10.45	1095
50	22.26	12.04	1081
60	20.70	13.60	1095
71	19.35	14.95	1088

$$k' \text{ (mean)} = 0.01093$$

$$k = k' \times 400/34.30 = 0.1275$$

\* Figures thus marked are not included in computation of averages.



*iso*Amyl iodide.

Temp. 30°. Zero = 39.15 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
120	38.30	0.85	1888
360	36.50	2.65	2017
770	33.95	5.20	1980
1140	31.90	7.25	1994
1620	29.60	9.55	1992
2200	27.20	11.95	1996
2820	25.05	14.10	1996
3160	24.05	15.10	1987

$$k' (\text{mean}) = 0.0001983$$

$$k = k' \times 400/39.15 = 0.002027$$

*sec.*-Hexyl iodide.

Temp. 50°. Zero = 36.90 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
15	34.30	2.60	5654
30	32.10	4.80	4948
45	30.15	6.75	4975
65	27.85	9.05	4999
85	25.95	10.95	4964
105	24.30	12.60	4939
135	22.10	14.80	4962
165	20.20	16.70	5009

$$k' (\text{mean}) = 0.004986$$

$$k = k' \times 400/36.90 = 0.05405$$

*n*-Heptyl iodide.

Temp. 40°. Zero = 38.95 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
40	37.10	1.85	1247
105	34.40	4.55	1260
175	31.90	7.05	1263
260	29.35	9.60	1260
360	26.85	12.10	1252
470	24.45	14.50	1262
590	22.40	16.55	1252
710	20.50	18.45	1268

$$k' (\text{mean}) = 0.001258$$

$$k = k' \times 400/38.95 = 0.01292$$

*n*-Octyl iodide.

Temp. 50°. Zero = 37.70 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
15	35.78	1.92	3578
35	33.55	4.15	3534
55	31.55	6.15	3543
80	29.40	8.30	3529
110	27.10	10.60	3556
150	24.58	13.12	3558
200	22.05	15.65	3549
260	19.60	18.10	3551

$$k' (\text{mean}) = 0.003550$$

$$k = k' \times 400/37.70 = 0.03767$$

*sec.*-Octyl iodide.

Temp. 30°. Zero = 39.00 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
75	37.80	1.20	4233
195	36.00	3.00	4274
395	33.40	5.60	4245
625	30.80	8.20	4259
900	28.10	10.90	4310
1255	25.60	13.40	4170
1648	23.05	15.95	4201
1880	21.60	17.40	4284

$$k' (\text{mean}) = 0.0004247$$

$$k = k' \times 400/39.00 = 0.004356$$

## Hexadecyl iodide.

Temp. 60°. Zero = 35.20 c.c.			
<i>t</i> (mins.).	( <i>a</i> - <i>x</i> ) c.c.	<i>x</i> .	<i>k'</i> × 10 <sup>3</sup> .
5	33.45	1.75	10280*
12	31.90	3.30	8620
22	29.55	5.65	8692
33	27.35	7.85	8702
45	25.40	9.80	8574
60	23.20	12.00	8620
80	20.85	14.35	8600
95	19.35	15.85	8624

$$k' (\text{mean}) = 0.008633$$

$$k = k' \times 400/35.20 = 0.09813$$

\* Figures thus marked are not included in computation of averages.

The further experiments demonstrating the effect of temperature on the velocity coefficient are summarised in the following table. Each experiment is duplicated.

SODIUM BENZYLOXIDE AND THE EFFECT OF TEMPERATURE, ETC. 1915

*Summary of Results Expressed as  $k \times 10^6$  at Various Temperatures.*

Iodide.	0°.	20°.	30°.	
Methyl .....	3844	51340	158900	
	3828	51600	160100	
	20°.	30°.	40°.	50°.
Ethyl .....	4143	14260	45560	137800
	4140	14200	45560	136000
	30°.	40°.	50°.	60°.
n-Propyl .....	5599	17580	51240	144000
	5489	17870	51140	143000
iso-Propyl .....	3314	10330	30430	82210
	3307	10380	30630	81300
n-Butyl .....	4012	13070	37750	102900
	4010	12880	37620	103300
iso-Butyl .....	5200	16350	48890	127500
	5215	16400	48910	128300
iso-Amyl .....	2027	7276	20960	51260
	2041	7242	20820	51400
sec.-Hexyl .....	5765	18320	54050	145700
	5771	18280	54100	146300
n-Heptyl .....	4007	12920	37740	101400
	4008	13030	37690	101800
n-Octyl .....	4005	12730	37670	98630
	4006	12750	37730	99600
sec.-Octyl .....	4356	13940	41370	113100
	4348	13970	41210	112900
Hexadecyl .....	4144	12750	36600	98130
	4140	12780	36200	98400

*Discussion of Results.*

The relationship between the reciprocal of the absolute temperature and the logarithm of the velocity constants is, with the exception of *iso*amyl iodide, best expressed graphically as a straight line, whilst the results at the highest temperature gives values slightly below such a straight line.

A simple relationship of this type can be represented by the equation

$$\log k_1 - \log k_2 = A(1/T_2 - 1/T_1),$$

where  $k_1$  and  $k_2$  are the velocities of reaction between an iodide and sodium benzyloxide at temperature  $T_1$  and  $T_2$ , respectively.

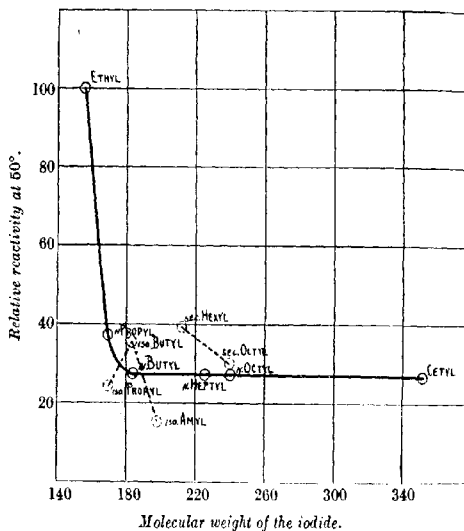
The results obtained by use of this equation are summarised in the following table, which shows the values for  $k_{40}$  and  $k_{60}$  calculated from the values of  $k_{30}$  and  $k_{50}$ , as compared with the results determined by direct experiment.

## 1916 HAYWOOD: THE REACTIVITY OF ALKYL IODIDES WITH

Iodide.	$k_{40^\circ} \times 10^6$ (calc.).	$k_{40^\circ} \times 10^6$ (obs.).	$k_{60^\circ} \times 10^6$ (calc.).	$k_{60^\circ} \times 10^6$ (obs.).
Methyl .....	5001*	5147*		
Ethyl .....	4577	4557	408.6*	414.3*
<i>n</i> -Propyl .....	1733	1772	15080	14450
<i>n</i> -Butyl .....	1276	1298	10470	10310
<i>n</i> -Heptyl .....	1275	1285	10460	10140
<i>n</i> -Octyl .....	1274	1274	10460	9911
Hexadecyl .....	1276	1276	9863	9826
<i>iso</i> Propyl .....	1041	1033	8390	8221
<i>iso</i> Butyl .....	1654	1637	13550	12790
<i>iso</i> Amyl .....	676.6	725.9	6030	5133
<i>sec.</i> -Hexyl .....	1829	1830	14970	14600
<i>sec.</i> -Octyl .....	1390	1395	11490	11300

\* Values of  $k_{20^\circ} \times 10^6$ .

FIG. 2.



The above tabulation shows that results obtained at varying temperatures are satisfactorily expressed by such an equation; which is deduced on the basis of the quantum theory.

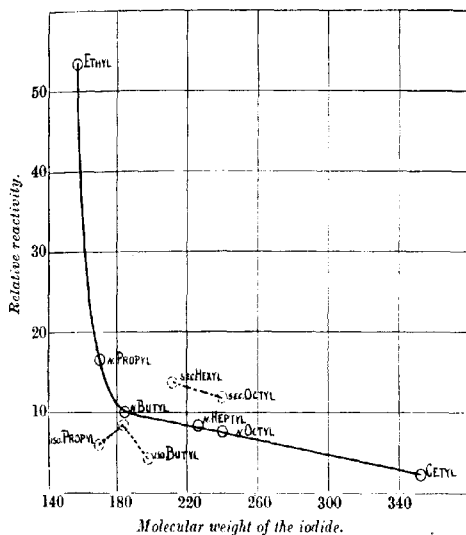
By comparison of the velocity coefficients of the different iodides at the same temperature we can obtain values for the relative reactivity.

SODIUM BENZYLOXIDE AND THE EFFECT OF TEMPERATURE, ETC. 1917

Iodide.	Relative reactivity at				
	20°.	30°.	40°.	50°.	60°.
Methyl .....	1248	1150			
Ethyl .....	100*	100*	100*	100*	[100]
<i>n</i> -Propyl .....		39.55	38.89	37.41	39.25
<i>n</i> -Butyl .....		28.18	28.48	27.58	28.00*
<i>n</i> -Heptyl .....		28.16	28.19	27.55	27.54
<i>n</i> -Octyl .....		28.15	27.96	27.54	26.93
Hexadecyl .....		29.11	28.00	26.74	26.75
<i>iso</i> Propyl .....		23.19	22.67	22.32	22.34
<i>iso</i> Butyl .....		36.59	35.94	35.73	34.74
<i>iso</i> Amyl .....		14.29	15.89	15.26	13.91
<i>sec</i> -Hexyl .....		40.53	40.16	39.52	39.67
<i>sec</i> -Octyl .....		30.59	30.61	30.16	30.70

\* Denotes standard of comparison.

FIG. 3.



The variation of relative reactivity, obtained on the basis of equal molecular entropy change, with molecular weight of the iodide.

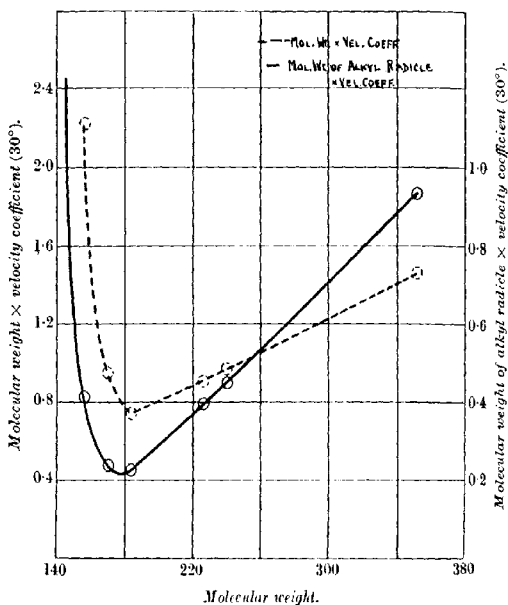
The relative reactivities at 50° in comparison with the molecular weight are shown in Fig. 2. The relative reactivity thus expressed varies somewhat with temperature.

The diagrammatic representation of the product of the molecular weight and the velocity coefficient plotted against the molecular

weight of the iodide is shown in Fig. 4, but it does not seem possible to reduce these values to a simple general expression.

Considering the case of two different iodides reacting independently with sodium benzyloxide, the variation of reactivity with temperature can be expressed by the equation  $k = k_0 e^{-A/T}$  where  $A/T$  = molecular entropy change in any given case in passing from the inactive to the active form. If the velocity coefficients for the reactions for the two iodides under the con-

FIG. 4.



dition of equal molecular entropy change are compared,  $A'/T' - A''/T'' = 0$ , and therefore  $k'/k'' = k_0'/k_0''$ . If the temperature is chosen to satisfy this condition, the relative activity is expressed as the ratio of the constants  $k'_0$  and  $k''_0$ , which are independent of temperature. It is clear also that the ratio  $k/k_0$  is the ratio of the velocity coefficient to the maximum velocity constant under the hypothetical condition of infinite temperature. In the case of two unimolecular reactions, this reduces to the simple result that the relative activity thus expressed is the ratio of the "in-

trinsic velocity coefficients" when the whole of the substances are in the active state. Also, the temperatures of equal molecular entropy change are the temperatures at which the "degree of activation" of the substances is the same. That these conclusions apply to the bimolecular reaction under consideration is shown by the following results.

Iodide.	A (mean).	A/T.	T (calc.).	Vel. coeff. $\times 10^6$ at $T^\circ$	Rel. react. (n-butyl iodide $-10^\circ$ ).	Mean rel. react.
Methyl .....	4510	15.25	295.8°	7216	72.28	71.87
		15.00	300.7	12690	72.36	
		14.75	305.8	22390	70.96	
Ethyl.....	4793	15.25	314.4	5274	53.53	53.6
		15.00	319.6	9354	53.53	
		14.75	324.9	16960	53.76	
n-Propyl .....	4765	15.25	312.5	1665	16.85	16.83
		15.00	317.7	2951	16.90	
		14.75	323.0	5284	16.75	
n-Butyl .....	4737	15.25	319.7	998.3	10.00	10.00
		15.00	315.8	1752	"	
		14.75	321.1	3155	"	
n-Heptyl .....	4716	15.25	309.2	836.6	8.54	8.52
		15.00	314.4	1496	8.49	
		14.75	319.7	2667	8.54	
n-Octyl .....	4703	15.25	308.6	763.8	7.63	7.64
		15.00	313.5	1337	7.73	
		14.75	318.8	2388	7.57	
Hexadecyl .....	4624	15.25	303.3	421.7	4.26	4.25
		15.00	308.2	746.4	4.28	
		14.75	313.4	1327	4.21	
isoPropyl .....	4695	15.25	308.0	588.8	5.87	5.90
		15.00	313.0	1033	5.90	
		14.75	318.4	1878	5.92	
isoButyl .....	4683	15.25	307.1	843.3	8.47	8.49
		15.00	312.1	1488	8.50	
		14.75	317.5	2685	8.51	
isoAmyl .....	4695	15.25	308.0	397.2	3.98	4.10
		15.00	313.0	729.5	4.14	
		14.75	318.4	1326	4.19	
sec.-Hexyl .....	4731	15.25	310.3	1358	13.61	13.67
		15.00	315.4	2399	13.70	
		14.75	320.7	4325	13.71	
sec.-Octyl .....	4750	15.25	311.6	1175	11.77	11.70
		15.00	316.6	2032	11.60	
		14.75	322.1	3698	11.72	

The independence of temperature of the relative reactivity is clearly shown in column six.

If we consider the variation of relative reactivity of the normal iodides studied, deduced on the basis of equal molecular entropy

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change as defined above, with molecular weight, we obtain a continuous curve (Fig. 3) which can be expressed by the general equation

$$ay^2 + bm^2 + cmy + dn + ey = 1,$$

where  $y$  is the relative reactivity and  $m$  the molecular weight. The constants have the values,  $a = -0.045907$ ;  $b = -0.036926$ ;  $c = -0.02030$ ;  $d = +0.02448$ ;  $e = +0.1023$ . This gives the value for the relative reactivity

$$-20.517n + 51.87 + (403.79n^2 - 1666n + 1754.2)^{1/2},$$

where  $n$  equals the number of methylene groups present in the iodide.

The experimental results obtained and the values calculated by aid of the above relationship are compared in the following table:

Iodide.	Relative reactivity.	
	Obs.	Calc.
Methyl .....	71.87	93.75
Ethyl .....	53.60	53.53
<i>n</i> -Propyl .....	16.83	16.94
<i>n</i> -Butyl .....	10.00	10.04
<i>n</i> -Heptyl .....	8.52	8.12
<i>n</i> -Octyl .....	7.64	7.74
Hexadecyl .....	4.25	4.12

With the exception of methyl iodide there appears to be good agreement.

## Summary.

(1) The reaction between the alkyl iodides and sodium benzyloxyde in ethyl-alcoholic solution is a bimolecular one of a special type in which the velocity of reaction is dependent on initial concentration.

(2) The presence of an excess of benzyl alcohol decreases the velocity coefficient, whilst a trace of water gives a slightly increased coefficient.

(3) The velocity of reaction increases with dilution, and the equation  $k_{r_1} - k_{r_2} = a \log v_1/v_2$  holds good for ethyl and *n*-propyl iodides up to at least dilution  $v = 10$ .

(4) The temperature coefficients of the reaction of alkyl iodides with sodium benzyloxyde in alcoholic solution are large; the ratios of the velocity coefficients for two temperatures differing by  $10^\circ$  are fairly constant for the series and lie between 3.04 and 3.08 approximately.

(5) The coefficients found for the three lower temperatures are in close agreement with the equation

$$\log k_1 - \log k_2 = A(1/T_2 - 1/T_1).$$

In the case of the highest temperature, the values are found to be slightly less than those required by the formula.

(6) The relative reactivities of the alkyl iodides with sodium benzyloxide in alcoholic solution are not completely independent of temperature, in the case of hexadecyl iodide the value crossing the value of the other iodides at the highest temperatures (Segaller's results show the same change).

(7) By comparison of velocity coefficients of the various alkyl iodides at the same temperature, results are obtained in fair agreement with previous investigations, for example, those of Hecht, Conrad, and Segaller. The values for methyl iodide do not agree with those of Segaller, neither do they support the anomalous reactivity of methyl iodide described by Burke and Donnan.

(8) The relative reactivities of the alkyl iodides studied are most conveniently expressed by comparison of their velocity coefficient under conditions of equal molecular entropy change.

The author wishes to express his indebtedness to the Principal, Mr. S. Skinner, and to the Head of the Chemical Department, Mr. J. B. Coleman, of this Institute, for the facilities given for this research, and also to Dr. J. C. Crocker for his unfailing interest.

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### CCXXIX.—*The Constitution of the Disaccharides.* *Part VI. The Biose of Amygdalin.*

By WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH.

SINCE the classical researches of Liebig and Wöhler on amygdalin and "oil of bitter almonds" (*Annalen*, 1837, **22**, 1), there have been repeated attempts to establish the structure of the sugar residue associated with mandelonitrile in this natural glucoside. It has been the endeavour of the present authors to elucidate this problem by the application of a method, described in earlier papers in this series, which has proved efficacious for determining the constitution of other disaccharides.

Liebig and Wöhler observed that alkalis hydrolyse the nitrile group of amygdalin to carboxyl with liberation of ammonia and formation of amygdalinic acid,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{O}\cdot\text{C}_{12}\text{H}_{21}\text{O}_{10}$ . This transformation has been shown by Dakin (*T.*, 1904, **85**, 1512) to

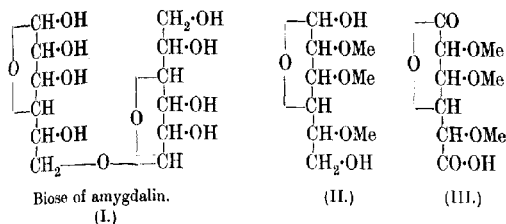


be accompanied by racemisation of the mandelic acid complex, the sugar residue being unaffected. With cognisance of these facts, this investigation was initiated by subjecting amygdalin to the methylating action of methyl sulphate in the presence of sodium hydroxide on the general lines previously indicated by the present authors.

Concurrently with the formation of amygdalinic acid by contact of the amygdalin with alkali, each of the exposed hydroxyl positions of the biose residue received a protecting methyl group, and the carboxyl group was also esterified. The product of this reaction was a new crystalline compound, namely, the methyl ester of heptamethyl amygdalinic acid (V), having  $[\alpha]_D^{25}$   $-51.7^\circ$  in ethyl alcohol.

Graded scission of this compound by dilute acid led to the isolation of three cleavage products, one recognisable as *dl*-mandelic acid, whilst the biose was represented by two partly methylated hexoses. With comparative ease, it was demonstrated that one of these hexose derivatives was tetramethyl glucose of the usual butylene oxide form (VI); the chief difficulty lay, however, in establishing the structure of the remaining hexose, which, on analysis, corresponded with a trimethyl glucose. That the latter was definitely a glucose of the butylene oxide form was shown by its ready conversion into the crystalline tetramethyl glucose which is the standard reference compound in this series. Precise allocation of positions to the methoxyl and free hydroxyl groups in this trimethyl glucose was thus the outstanding problem, since the exposed hydroxyl groups represent positions newly disengaged from the previous linking in the biose itself and also from its union with the aromatic complex.

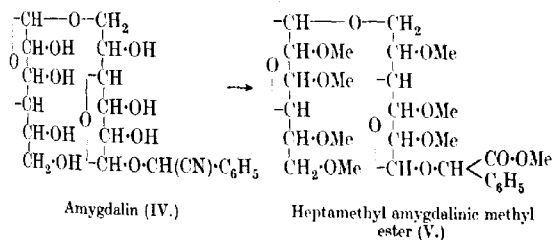
There are four possible formulæ for such a trimethyl glucose; one of the four compounds is crystalline and has already been isolated from methylated lactose and cellobiose (T., 1921, 119, 200). But the trimethyl sugar in the present case was a viscous liquid, which did not crystallise on nucleation with the crystalline variety. Application of Fischer's method of glucoside formation gave, however, a crystalline trimethyl  $\beta$ -methylglucoside melting at  $94.5^\circ$  and distilling at  $109^\circ/0.06$  mm. Hydrolysis with dilute acid regenerated the free sugar. Oxidation of this with dilute nitric acid led to the isolation of a product which furnished an important clue to its constitution. The trimethyl glucose was quickly oxidised to a dibasic acid, showing that the two terminal positions in the hexose chain were unoccupied by methyl groups, and this acid was converted into the corresponding lactone of trimethyl saccharic acid (III).

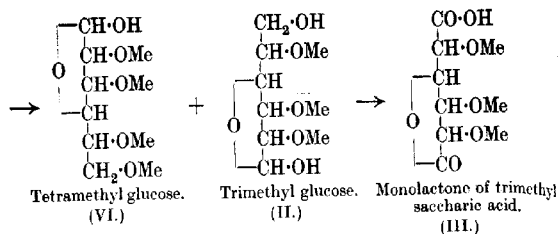


This last-named compound had already been encountered during our earlier investigation on maltose (Haworth and Leitch, T., 1919, 115, 809), and such a lactone could only have been produced by oxidation of a trimethyl sugar of the constitution II. The evidence here adduced, together with the facts enumerated in the following paragraph, serves to assign the formula I to the biose of amygdalin, which, apart from the stereochemical reservations, is structurally identical with maltose.

Complementary evidence is needed to support the view that the amygdalin-biose belongs to the series of reducing sugars. Gajda (*Compt. rend.*, 1910, 150, 793) claims that the sugar is of the non-reducing type like trehalose. If this observation be correct, then the mandelonitrile glucoside (prunasin), obtained by Fischer (*Ber.*, 1895, 28, 1508) from amygdalin by graded enzyme action, must contain a free reducing group in the sugar residue. But Fischer states that this compound does not reduce Fehling's solution. Moreover, Fischer and Bergmann (*Ber.*, 1917, 50, 1051) have recently synthesised the stereoisomeride of prunasin, namely, sambunigrin, by a series of steps which exclude the possibility of a free reducing group remaining in the glucoside.

The complete formulation of amygdalin may then be given (IV), and the following scheme shows the stages by which the proof has been developed in the course of the present work :—





The disaccharide of amygdalin has therefore the structure of maltose and quite definitely cannot be cellobiose. For the *stereochemical* formulation of this maltose structure we are dependent on the researches of other workers on the selective action of enzymes, and here the results, if not conflicting, are certainly anomalous. Their results favour the view that the amygdalin-biose is a glucose  $\alpha$ -glucoside. We have shown that this has the structure of maltose and therefore, on this reasoning, the biose itself must be maltose and amygdalin is mandelonitrile  $\beta$ -maltoside (that is, mandelonitrile  $\beta$ -glucose  $\alpha$ -glucoside). On the other hand, amygdalin is completely hydrolysed, not by maltase, but by emulsin; but it is explained that the specific action usually attributable to emulsin is operative here at the  $\beta$ -linking adjoining the aromatic residue. The cleavage of the biose into glucose is said to be the function of amygdalase present also in emulsin, but not responsible for the hydrolysis of  $\beta$ -glucosides.

The conclusion we have definitely drawn assigning to the biose of amygdalin the same structural formula as maltose is contrary to the anticipated result, having regard to the statements of other recent workers based on studies of enzyme action and rate of hydrolysis. Should it ultimately be the case that the stereochemical representation of the biose is found to be that of a glucose- $\beta$ -glucoside, this cannot, of course, affect the structural formula we have herein ascribed to the sugar, but it may point to the identity of the amygdalin-biose with isomaltose or gentiobiose. Up to the present, the structural formulæ of these last two disaccharides have not been determined, although their investigation is proceeding in these laboratories.

#### EXPERIMENTAL.

##### *Methylation of Amygdalin. Isolation of the Methyl Ester of Heptamethyl Amygdalonic Acid.*

The amygdalin required for the present work was extracted with hot alcohol from bitter almond meal and was obtained after

recrystallisation from ethyl alcohol as colourless prisms melting at  $215^{\circ}$  and showing  $[\alpha]_D - 39.8^{\circ}$  in aqueous solution ( $c = 1.54$ ).

Amygdalin (25 grams) was dissolved in the minimum volume of water and methylated by the general method described by one of us (T., 1915, 107, 11), using 50 grams of sodium hydroxide dissolved in 160 c.c. of water, and 71 grams of methyl sulphate. The reaction was conducted at  $70^{\circ}$  during two and a half hours and was accompanied by a good deal of frothing, due to the elimination of ammonia. Thereafter the temperature was raised to  $100^{\circ}$  for three-quarters of an hour. At this stage of the operations, it was clear that, whilst partial methylation of the sugar residue had occurred, the nitrile group had simultaneously undergone hydrolysis to carboxyl by the agency of the alkali; consequently the product was in the form of a sodium salt of methylated amygdalinic acid. To the clear aqueous solution an exactly sufficient quantity of dilute sulphuric acid was added to liberate the organic acid from its salt. Excess of mineral acid was carefully avoided. Much of the sodium sulphate was removed from solution by means of alcohol, and the filtrate carefully concentrated under diminished pressure until only a viscous gum remained containing some sodium sulphate. The methylation was repeated with this product, using the same quantity of each reagent as before. At the end of this second methylation the aqueous solution was cooled, acidified with dilute sulphuric acid, and the pale yellow oil which now appeared on the surface extracted with chloroform. On the removal of the solvent, a yellow syrup remained which was acid and weighed 19 grams (Found: OMe = 30.2 per cent.).

A further quantity of the product may be recovered from the aqueous solution on concentration. The partly methylated amygdalinic acid was digested with silver oxide (25 grams) and methyl iodide (40 grams). From this further methylation, which was again repeated, a pale yellow, viscid syrup was isolated by the usual procedure. This was dried in a vacuum at  $120^{\circ}$  and gave OMe = 39.8 per cent.

It was interesting to find that this product, which no longer showed an acid reaction, distilled smoothly under 0.02 mm. from a metal-bath heated at  $270^{\circ}$ . The colourless distillate, which was viscid, partly crystallised on keeping. On recrystallisation from light petroleum, the whole of the distillate appeared as minute, colourless needles melting at  $91^{\circ}$ . Later, it was found possible to isolate this crystalline product from the crude syrup without distillation (Found: C = 57.01; H = 7.51; OMe = 40.8.  $C_{28}H_{44}O_{13}$  requires C = 57.14; H = 7.48; OMe = 42.2 per cent.).

These analytical data correspond with those required for methyl

heptamethylamygdalinate and show that the disaccharide residue is retained in this compound, the seven available hydroxyl groups of which are protected by methyl groups. Further methylation failed to introduce a greater number of methyl residues. The specific rotation of this substance in different solvents is given below :—

Solvent.	c.	$[\alpha]_D^{16}$ .
Methyl alcohol .....	2	— 49.3°
Absolute ethyl alcohol .....	2	— 51.7
Acetone .....	2	— 50.8
* Water (containing 20 per cent. of ethyl alcohol) .....	0.7	— 55.7

\* The compound is sparingly soluble in water.

#### *Hydrolysis of the Methyl Ester of Heptamethylamygdalinic Acid.*

Comparative experiments with various concentrations of mineral acids indicated that the most satisfactory result was obtained by using 5 per cent. aqueous hydrochloric acid at 95°.

The material undergoing hydrolysis was initially sparingly soluble in aqueous acids. Preliminary attempts were therefore made to effect hydrolysis with 5 per cent. hydrochloric acid in 30 per cent. aqueous alcohol. The boiling point of this mixed solvent was found to be too low to effect complete hydrolysis; a very slight change occurred in the polarimetric readings during four hours, the original value,  $[\alpha]_D$  — 55°, falling only to  $[\alpha]_D$  — 32°. A larger proportion of the material was dissolved in 8 per cent. aqueous hydrochloric acid containing 20 per cent. of alcohol, and hydrolysis was complete in one and three-quarters hours, the final specific rotation being + 56°. Again, with 16 per cent. aqueous acid, digestion for half an hour showed a change from  $[\alpha]_D$  — 56° to + 44°, but in the latter two cases slight darkening of the solution occurred. On the other hand, much more dilute hydrochloric acid (1.5 per cent. aqueous) required a prolonged digestion at 100° to change the initial value to  $[\alpha]_D$  + 25°, and in this experiment one-third of the original material, having remained undissolved, was recovered unchanged.

The following are the figures recorded in a typical experiment conducted with 10 grams of methylated amygdalinic ester, using in this case 5 per cent. aqueous hydrochloric acid at 95° for seven hours :—

Time in hours.	$[\alpha]_D$ .	Corrected values for $[\alpha]_D$ for quantity of substance dissolved.	Time in hours.	$[\alpha]_D$ .	Corrected values for $[\alpha]_D$ for quantity of substance dissolved
0.5	— 1.0°	— 2.9°	5.0	27.6°	42.5°
1.0	+ 7.4	+ 11.4	6.5	47.9	73.7
1.5	14.8	22.8	7.0	constant	(c = 1.35)
2.0	21.1	32.5			

In this experiment approximately 3.5 grams of the original material were recovered unchanged, and this was used in a subsequent hydrolysis. Later, it was found that the addition of a little acetone aided dissolution in the initial stages, and led to the complete hydrolysis of the whole of the material in one experiment.

*Isolation of dl-Mandelic Acid and Tetramethyl and Trimethyl Glucoses.*

The acid solution, after hydrolysis, was neutralised with barium carbonate, filtered, and concentrated under diminished pressure at 40°, the mineral salts being removed from time to time by the addition of alcohol. An agglutinous solid residue remained on complete evaporation of the solvent. Trituration of this cake of material with chloroform separated the product into two parts: a solid, which was found to be barium mandelate, and a chloroform solution of methylated hexoses. Solution of the white solid in dilute hydrochloric acid, followed by extraction with ether, led to the isolation of free mandelic acid which, after recrystallisation from benzene, appeared in the form of large, colourless prisms melting at 116–118°, and was optically inactive. A mixture of this product with authentic *dl*-mandelic acid (m. p. 118°) showed no depression of the melting point (Found: C = 62.75; H = 5.22 per cent.).

Racemisation of the mandelic acid residue had therefore occurred during the preceding operations (compare Dakin, *loc. cit.*).

The chloroform extract yielded a colourless syrup, which was digested repeatedly with light petroleum. This treatment effected separation into two approximately equal portions and, from this solvent, crystals melting at 84° were isolated, whilst the insoluble portion remained as a viscid liquid. Purification of the crystals from light petroleum containing a trace of ethyl acetate yielded a compound melting at 89°, and this showed all the properties of butylene-oxidic tetramethyl glucose. A mixed melting-point determination with an authentic specimen along with the analytical and polarimetric data confirmed its identity (Found: C = 50.76; H = 8.6; OMe = 51.39 per cent.). A specific rotation in water showed the value  $[\alpha]_D + 88.3^\circ$ , falling after catalysis to the recognised equilibrium value,  $[\alpha]_D + 83.2^\circ$ .

Remaining from the extraction with light petroleum was the insoluble portion of viscid liquid, which was subjected to distillation in a high vacuum, when it was found that this substance distilled at 155–170°/0.3 mm. A methoxyl estimation gave results indicating that this substance was essentially a trimethyl

hexose containing, however, some trimethyl glucosan (Found: OMe = 43.8 per cent.).

Accordingly, the whole of the distillate was digested for forty-eight hours at  $114^{\circ}$  in a sealed vessel with 0.5 per cent. methyl-alcoholic hydrogen chloride. Thereafter, neutralisation with silver carbonate and evaporation gave rise to a colourless liquid which distilled smoothly at  $111^{\circ}/0.07$  mm. and showed  $[\alpha]_D + 93.9^{\circ}$  ( $c = 3.3$ ) in aqueous solution, and  $n_D 1.4594$ . This compound was unaffected by boiling with Fehling's solution (Found: C = 50.72; H = 8.5; OMe = 51.6.  $C_{10}H_{20}O_6$  requires C = 50.84; H = 8.47; OMe = 52.5 per cent.).

The boiling point and specific rotation indicated that this trimethyl methylglucoside was a mixture of  $\alpha$ - and  $\beta$ -forms (compare Irvine and Oldham, T., 1921, **119**, 1758; Haworth, T., 1915, **107**, 13). On hydrolysis with 2.5 per cent. aqueous hydrochloric acid at  $95^{\circ}$ , another specimen of the glucoside was transformed into the free sugar, and during this process the following polarimetric data were recorded:—

Time (mins.)	0	60	120	180	270	330	380
$[\alpha]_D$ .....	+81.3°	85.3°	82.7°	78.5°	74.3°	71.9°	71.3°
				( $c = 5$ )			constant

Following isolation in the usual way, the free trimethyl glucose readily reduced Fehling's solution and showed  $n_D 1.4678$  for the dried syrup.

On another occasion, the portion of the material representing the trimethyl hexose was digested for twelve hours at  $110^{\circ}$  with 0.5 per cent. methyl-alcoholic hydrogen chloride, following throughout the conditions established by Fischer for glucoside formation. Isolation of the product by the usual method gave a colourless liquid, distilling at  $109^{\circ}/0.06$  mm., which soon crystallised. Purification from light petroleum gave colourless needles, melting at  $94.5^{\circ}$ , representing the pure trimethyl  $\beta$ -methylglucoside as distinct from the mixture of  $\alpha$ - and  $\beta$ -stereoisomerides described in the preceding paragraphs. This was identical in all respects with the compound isolated by Irvine and Oldham (*loc. cit.*), although the melting point was slightly higher. On hydrolysis with 8 per cent. aqueous hydrochloric acid for half an hour, the free trimethyl glucose was regenerated.

When the trimethyl methylglucoside was subjected to further methylation by Purdie's reagents, a fifth methyl group was introduced. Hydrolysis of this product gave rise to the crystalline tetramethyl glucose of the usual butylene oxide form. Proof was thus furnished as to the oxide linking in the trimethyl glucose, which is definitely butylene-oxidic.

*Oxidation of Trimethyl Glucose.*

This sugar, obtained from the hydrolysis of its glucoside as described in the previous section, was oxidised with dilute nitric acid (*d* 1.2) by heating for six and a half hours at 68°. The usual methods for the removal of the nitric acid and water having been applied, the residue was dried in a high vacuum, when a pale yellow syrup remained (Found: C = 46.08; H = 6.28; OMe = 40.1.  $C_9H_{14}O_7$  requires C = 46.15; H = 5.98; OMe = 39.7 per cent.).

On titration with *N*/10-alkali, the compound showed at first the behaviour of an organic acid, and latterly of a lactone. By heating for a few minutes with excess of alkali, followed by neutralisation with *N*/10-acid, it was observed that 0.1242 gram of the substance required 10.47 c.c. of *N*/10-sodium hydroxide, whilst the monolactone of trimethyl saccharic acid ( $C_9H_{14}O_7$ ) requires 10.6 c.c. (compare Haworth and Leitch, *loc. cit.*). The specific rotation of this monolactone in 50 per cent. aqueous ethyl alcohol showed +69.2° initially, falling to +51.2° after one hundred hours.

The authors express their thanks to the Carnegie Trust for the award of a research assistantship to one of them during the initial stages of this investigation, which was begun in the laboratories of the United College, University of St. Andrews. They are also grateful to the Chemical Society for a grant for materials. For assistance in the preparation of materials required in this research we are indebted to Mr. Birkett Wylam, a student in training under the Department of Scientific and Industrial Research.

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CCXXX.—*Amylases of the Cereal Grains—The*  
“Insoluble” Amylase of Barley.

By JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON.

IN previous papers (Baker, T., 1902, **77**, 1177; Baker and Hulton, *ibid.*, 1921, **119**, 805), the differences in the character of the amylase in some ungerminated and germinated cereals were described. One fundamental distinction is the production of maltose and  $\alpha$ -amylodextrin possessing a blue iodine reaction when the amylase of ungerminated cereals is allowed to act on gelatinised starch, whereas a germinated cereal produces, under similar conditions,



maltose and a series of dextrans of decreasing molecular complexity which do not react with iodine.

For some years past it has been recognised that ungerminated cereals contain more amylase than is yielded by aqueous extraction in the cold, and Ford and Guthrie (*J. Inst. Brewing*, 1908, **14**, 61) elaborated this point by showing that an enhanced degree of amylolytic activity of barley could be rendered evident by one or all of the following methods: (a) Allowing the solid barley substance instead of its aqueous extract to act on starch, (b) autodigestion: that is, the preparation of the aqueous extract for a prolonged time at a temperature of 30°, (c) the addition to the barley during such autodigestion of certain salts and proteins, (d) the addition to the barley during autodigestion of the active proteolytic enzyme papain. The filtrates obtained from these digestions were allowed to act on soluble starch at 40° for one hour under conditions precluding the formation of more than 35 per cent. of maltose by weight of the starch employed (Kjeldahl, *Compt. rend. Trav. Lab., Carlsberg*, 1879, **1**, 109) and the weight of maltose so formed was taken as a measure of the amount of amylase present. These workers concluded that the increases in amylolytic activity obtained by the use of papain were due to liberation and solution of the colloidal enzyme and to its protection from destruction in an aqueous medium. When ungerminated barley is treated with saline or other solutions, the complex protein groups decompose or dissociate to some extent, the active amylase being liberated. Should, however, there be an insufficient amount of amphoteric substances (proteins and salts) present, such amylase is gradually destroyed to a degree dependent on the hydrogen-ion concentration of the medium and the duration of the exposure.

Throughout Ford and Guthrie's work, the activating effect of autodigestion, papain, etc., was studied upon the entire barley material, which, of course, contained water-soluble amylase. Any increase in amylolytic activity so observed would therefore include the effect of such treatment on this soluble amylase as well as that caused by any production, protection, or liberation of otherwise insoluble amylase.

At this point, it will be convenient to refer to some work we published (*Rep. Brit. Assoc.*, 1909) on the action of the enzymes of malt on ungerminated barley. We showed there was an increase in the diastatic activity of barley when digested in an aqueous medium with malt, and gave reasons for our belief that this could be accounted for by the presence of a proteolytic enzyme in the malt. It was hoped a continuation of the work might be the means of throwing further light on some of the problems associated with germination.

The use of malt as a source of the proteolytic enzyme has its disadvantages, since it is always accompanied by malt amylase and therefore involves the complication of control conversions, whereas the employment of a preparation of papain—which we have assured ourselves is entirely free from amylase—avoids these. The remainder of the work to be described has accordingly been carried out with papain.

Since Ford and Guthrie (*loc. cit.*) have shown that an active amylase is liberated from barley by papain, we thought it possible that the mechanism of the production of amylase in germinating barley might be further elucidated by allowing papain to act, not on the entire barley, but on barley which had been successively treated with suitable solvents in order to effect the elimination of the different proteins. By such means it was hoped to identify the particular protein group associated with the amylase liberated by papain. We accordingly autodigested barley first with water, thereby extracting the albumins and soluble amylase, the residue was next extracted with 10 per cent. sodium chloride solution to remove the globulin edestin, and a final extraction with 75 per cent. alcohol eliminated hordein. Portions of these three residues were suspended in water, and further autodigested alone or with the addition of papain, the mixtures being kept at 30–33° for twenty hours in presence of a little toluene. A portion of the filtrate was then allowed to act on soluble starch for one hour at 40° and the amount of maltose so produced determined. The experimental evidence cited below shows that papain can liberate amylase from the water-extracted residue, and to a very slight extent from the residue after salt extraction (globulin-free material), whilst that portion from which hordein had been removed by alcohol showed no such activity.

#### EXPERIMENTAL.

Finely ground barley which had a diastatic activity of 22° Lintner was extracted for twenty-four hours with water containing a little toluene at air temperature, pumped dry, and again extracted for another twenty-four hours with water at 35° (autodigestion). This residue, which contained 54 per cent. of moisture, had a Lintner value of only 0.22° on dry matter, thus showing that practically all (99 per cent.) the soluble amylase had been removed. Before proceeding with the examination of this residue by extraction with salt and alcohol, a starch conversion was made to determine the general character of the amylase liberated when barley so extracted was submitted to digestion with papain. A portion was accordingly digested with 10 per cent. of its weight of papain for two hours at 37° in the presence of water; 200 c.c. of 2 per cent. soluble

starch were added to it and the conversion allowed to proceed for one hour at 21°. The reducing power in terms of maltose per 100 grams of starch was 50 per cent., the iodine reaction being blue. When fractionated with alcohol in the usual manner, crystallisable maltose and  $\alpha$ -amylodextrin were readily isolated in a state of purity. The newly liberated amylase responsible for this conversion is thus clearly of the barley type; it does not liquefy starch paste, and in no way resembles the characteristic enzyme produced when barley is germinated. Even when the time of digestion with papain was extended from two hours to four days, an identical type of conversion resulted.

Having shown that by such treatment a notable quantity of amylase is liberated, it was decided to continue the investigation on a quantitative basis by submitting the residues from the various extractions (water, salt, alcohol) to the test of maltose production under strictly defined conditions, and for this purpose those described by Ford and Guthrie (*loc. cit.*) were adopted, namely, the measurement of the maltose produced from excess of soluble starch for one hour at 40°, the results being recorded as grams of maltose per gram of dry barley.

Treatment.	Grams of maltose produced per gram of dry material			
	(1) Original barley.	(2) Residue after aqueous ex- traction under auto- digestion conditions.	(3) Material as in col. 2 after extraction with 75% alcohol.	(4) Material as in col. 2 after extraction with 10% NaCl.
Autodigestion with water 20 hours at 33° .....	6.27	2.02	0	0.16
Autodigestion with the addition of papain ...	11.2	4.31	0	0.83

Ten grams of the material after successive extractions with water, sodium chloride, and alcohol in the manner described were digested with (a) 125 c.c. of water, (b) 125 c.c. of water containing 0.3 gram of papain, for twenty hours at 33° in the presence of toluene. The digests were then filtered and a suitable volume was added to 70 c.c. of water containing 2 grams of dry soluble starch in solution. The conversions were maintained at 40° for one hour, at the end of which time the reaction was stopped by dilute soda, the whole cooled, made up to 100 c.c., and the maltose estimated by the use of Fehling's solution. From this figure was calculated the weight of maltose formed per gram of dry material. In all cases, the volume of the digest added to the soluble starch solution was so arranged that the reducing power did not exceed 25 per cent. of maltose on the starch used. It is only by taking such precautions

that the maltose produced becomes a true measure of the amount of amylase present. For purposes of comparison, the original barley used has been included in the table. Corrections were necessary for the reducing action of the papain and of the sugars in the barley.

These results show that barley previously submitted to a prolonged autodigestion in water (col. 2) is capable of yielding a further quantity of soluble amylase if it be again digested either with water alone or with papain, and it is probable that the liberation of amylase under such conditions would be continuous until all of it is removed. The effect of papain is very marked, the increased amount of amylase liberated exceeding twice that yielded by autodigestion alone.

A further point brought out is that no amylase can be liberated in a material from which the hordein fraction has been removed, and, in view of this, it might be anticipated that it is mainly from this protein group that papain-liberated amylase arises. Attempts to produce liberation of amylase by means of papain from a preparation of hordein itself made from barley were unsuccessful—a result in agreement with a similar attempt by Ford and Guthrie (*loc. cit.*), but we differ from these workers with regard to the behaviour of the hordein-free barley residue left after alcohol extraction, for they recorded a considerable amylolytic activity from such material on treatment with papain. It is possible, however, that the cause of the discrepancy is to be found in the fact that our material was extracted with water before treatment with alcohol, whereas Ford and Guthrie's barley was apparently extracted direct with alcohol only, and thus some amylase soluble in water but not in alcohol may have been left behind to function as the source of the papain-activated enzyme they found.

It appeared to us likely that this question might be attacked from a slightly different standpoint with the view of determining whether the amylolytic activity rendered available by the use of papain was really present in the barley substance all the time but in the form of an insoluble zymogen or enzyme-complex which the papain broke down, or whether such additional amylase was an actual cleavage-product of some protein liberated by the proteolytic action of the papain. If the former is the truth, then it would appear probable that papain would produce no amylase if the original barley were previously heated so as to destroy any existing enzyme before the digestion with papain, whereas if the new amylase is in truth a function of some proteolytic cleavage product, then it should be possible to produce it by acting on "dead" or heated barley protein. An experiment to test this point was made

by acting on boiled or heated ( $120^{\circ}$ ) barley with papain under autodigestion conditions. The results, however, were negative and therefore it must be concluded that when amylase is liberated by papain the enzyme was pre-existent in the barley as a complex which was broken down by proteolytic action.

The conception of amylase as a cleavage-product formed as the result of proteolytic action on a non-amylolytic substrate is an attractive one, and does not seem to have been directly suggested by Ford and Guthrie, who lean more to the "protective" and "liberation of occluded enzyme" views of papain action, but in view of this last experiment together with our failure to obtain amylase by the action of papain on hordein, it would seem necessary to abandon it, and we must fall back on Ford's alternative hypothesis that the appearance of additional amylase when papain is employed is due to the proteolytic breaking-down of some complex formed by amylase with a protein substance. In any case so far as we have found, such liberated amylase is always and only of the barley type, which fact unfortunately throws no light on the appearance during the germination of barley of the characteristic malt amylase with its strong liquefying action towards starch paste, together with the non-production of the  $\alpha$ -amylodextrin with its blue iodine reaction.

#### *Conclusions.*

(1) The water-insoluble amylase of barley which is rendered soluble by proteolytic action (papain) is associated with the alcohol-soluble group of proteins (hordein).

(2) Since papain does not liberate an amylase from isolated hordein, or from barley which has been either boiled or heated to  $120^{\circ}$ , it follows that papain liberates amylase in virtue of its capacity to break down a pre-existent insoluble enzyme complex.

(3) Such amylase, when thus liberated by papain, exhibits the characteristic properties of the soluble amylase of barley.

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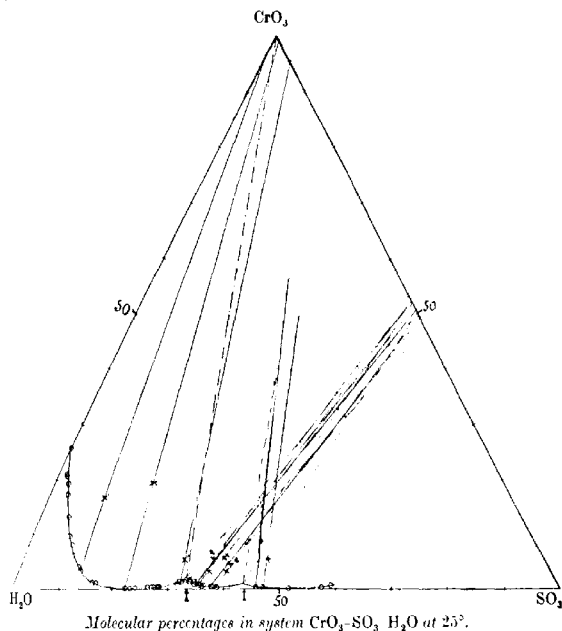
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### CCXXXI.—*The System Chromium Trioxide-Sulphur Trioxide-Water.*

By LIONEL FELIX GILBERT, HAROLD BUCKLEY, and  
IRVINE MASSON.

GAY-LUSSAC (*Ann. chim. phys.*, 1821, [ii], **16**, 102) mixed sulphuric and chromic acids and obtained red quadrangular prisms to which

he gave a formula corresponding with  $\text{CrO}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O}$ . Fritsche (*J. pr. Chem.*, 1840, **19**, 176) ascribed Gay-Lussac's results to contamination of solid chromium trioxide with sulphuric acid; Bolley (*Ann. chim. pharm.*, 1845, **56**, 113) gave Gay-Lussac's formula to an ochre-yellow, pasty substance obtained in a similar way. Schrötter (*Pogg. Ann.*, 1843, **59**, 616) examined a yellowish-brown substance which he could not isolate completely, and attributed to it the probable formula  $\text{CrO}_3 \cdot 3\text{SO}_3$ . Pictet and Karl (*Bull.*



*Soc. chim.*, 1908, [iv], **3**, 1114) prepared, by the action of sulphur trioxide on chromium trioxide heated in a sealed tube, a yellowish-brown mass, to which they gave the formula  $\text{CrO}_3 \cdot \text{SO}_3$ . All these investigators note the instability of the substances in air, and the liberation of chromium trioxide by the action of moisture.

Having observed the peculiar behaviour of sulphuric acid towards chromic acid, we have made a partial survey of the condensed ternary system  $\text{CrO}_3$ - $\text{SO}_3$ - $\text{H}_2\text{O}$  by carrying out measurements of the solubilities of chromium trioxide at  $25^\circ$  and at  $45^\circ$  in sulphuric acid of varying concentration, accompanied by direct and indirect analyses of the solid phases.

Both isotherms are almost coincident, and the data, most of which are plotted in the diagram, show that there are three distinct regions, each with a minimum of solubility. The first region corresponds with chromium trioxide as the solid phase; the minimum solubility, 0.3 per cent. by weight, occurs in aqueous sulphuric acid of 70 per cent.  $\text{H}_2\text{SO}_4$ , and the transition to the next stage occurs in acid of concentration 85 per cent.  $\text{H}_2\text{SO}_4$ . Supersaturated solutions of chromium trioxide may, however, be formed, even in highly concentrated acid. From this strength up to that of acid containing at most 95 per cent.  $\text{H}_2\text{SO}_4$ , the solid phase is a compound  $\text{CrO}_3\cdot\text{SO}_3$ . With higher concentrations of sulphur trioxide the third region is entered and the solid again changes its composition, probably becoming  $\text{CrO}_3\cdot\text{SO}_3\cdot\text{H}_2\text{O}$ . The solubilities of the complex compounds are small, but are sufficient to give a dark brown colour to the liquids. These substances are so finely divided as to be very troublesome to examine; the compound  $\text{CrO}_3\cdot\text{SO}_3$  is usually brown and minutely crystalline, but it may appear as a tawny amorphous sludge, and always does so when deposited from the higher concentrations of sulphuric or fuming sulphuric acid. The third solid is also tawny and apparently amorphous. Both forms are excessively hygroscopic, and liberate scarlet chromium trioxide on exposure.

The attainment of equilibrium in these liquids, where the viscosity is not inconsiderable and the precipitates are in the form of slime, is slow. Continuous agitation for at least three days was allowed before examining the samples; several experiments were made in which agitation was carried on for a fortnight without causing any change in the appearance of the solid or in the character of the results; equilibrium was approached from both sides, and, it is believed, was attained in practically every case as far as the nature of the material will permit.

#### EXPERIMENTAL.

1. *Procedure.*—Two isotherms were studied, one at  $25.0^\circ$  and one, in less detail, at  $45.0^\circ$ . The components, concentrated or fuming sulphuric acid and chromium trioxide, were free from impurities by all ordinary tests. They were mixed in suitable proportions and put in glass tubes of about 100 c.c. capacity, which were then quickly sealed and transferred to a thermostat, where they revolved. Before samples were withdrawn, the tubes were placed upright in the thermostat so that the solid should segregate. Each tube was then opened and a sample of the liquid phase rapidly taken in a warmed pipette and was used to fill a density-bottle supported in the thermostat; the remaining liquid was decanted off as far as possible and some of the residual wet

solid was rapidly transferred to a weighing-bottle. After being weighed, the samples were analysed.

2. *Method of Analysis.*—Several methods were tested and rejected, and the following was finally adopted. In one portion of the mixture, suitably diluted, the total acidity was determined with *N*/10-barium hydroxide, using as indicator phenolphthalein, the colour-change of which is not interfered with by the pale yellow precipitate of barium chromate. In a second portion, the chromium trioxide was estimated iodometrically. Sulphur trioxide and water are thus estimated by difference. Careful tests showed that the method for total acidity gives results accurate to about 0.1 per cent.; and although a volumetric and differential method has obvious disadvantages, no other was found to be adequate for the present purpose.

3. *Compositions of the Solid Phases.*—(a) Direct analysis. Samples of amorphous solid obtained from mixtures of chromium trioxide and 97 per cent. sulphuric acid were analysed after suction with dry air and storage on a porous plate; but although sulphur trioxide was evidently a principal constituent, they were found to be insufficiently free from liquid. A further preparation was therefore well washed in a dry atmosphere with specially anhydrous ether, in which both chromium trioxide and sulphuric acid are separately soluble. In the subsequent analyses, a small amount of the material was reduced by adherent ether when it was dissolved in water, which would augment the apparent water-content at the expense of the content of chromium trioxide. The results gave molecular ratios  $\text{CrO}_3 \cdot \text{SO}_3 \cdot \text{H}_2\text{O} = 1 : 1.22 : 1.40$  and  $1 : 1.33 : 1.52$ . No other direct analyses were made.

(b) Indirect determinations were made by analysing the wet solids, the compositions of which are given in the tables with those of the corresponding liquids. In the figure, the lines joining the compositions of solids and liquids are too numerous for all to be reproduced. It is certain, however, that the solid phase is  $\text{CrO}_3$  up to a molecular concentration of about 32.5 per cent. of sulphur trioxide in the liquid, and that it is essentially  $\text{CrO}_3 \cdot \text{SO}_3$  from that point on to approximately 43 molecular per cent. of sulphur trioxide. What remains uncertain, owing to the difficulties attending the exact analysis of "solids" which were in reality chiefly liquid, is whether this compound may not contain small quantities of either component adsorbed or in solid solution, the extremes of composition of the dry solid being  $\text{CrO}_3 \cdot 1.15\text{SO}_3$  and  $\text{CrO}_3 \cdot 0.88\text{SO}_3$ ; but, from the unsystematic nature of the deviations, we incline to the belief that they arise from this experimental cause and that the actual solid is  $\text{CrO}_3 \cdot \text{SO}_3$ . As to the region of liquids richest in sulphur trioxide, there is no doubt of the occurrence of a further



change in the solid phase; but, for the reasons already mentioned, and because only two samples at 25° and one at 45° were examined, the composition of the new phase remains in doubt. These data prove that it cannot be the compound  $\text{CrO}_3\cdot\text{SO}_3$ , already defined; they do not quite exclude the possibility of its being an amorphous variety of chromium trioxide itself, but they harmonise best with the supposition that the third solid has the composition  $\text{H}_2\text{O}\cdot\text{CrO}_3\cdot\text{SO}_3$ , intermediate between dichromic and disulphuric acids.

TABLE I.

*Molecular percentages and densities at 25°.*

Liquid.			Wet solid.		Liquid.			Wet solid.	
$d_4^{25}$	$\text{SO}_3$	$\text{CrO}_3$	$\text{SO}_3$	$\text{CrO}_3$	$d_4^{25}$	$\text{SO}_3$	$\text{CrO}_3$	$\text{SO}_3$	$\text{CrO}_3$
—	0	25.78	—	—	1.788	33.17	1.58	34.61	6.83
1.678	1.47	21.10	—	—	1.803	33.74	1.02	—	—
1.669	1.55	20.69	—	—	1.808	34.42	1.38	35.30	5.95
1.650	2.53	19.27	—	—	1.896	34.29	0.97	35.34	13.75
1.626	3.34	17.41	—	—	—	34.54	0.82	—	—
1.579	5.73	13.20	—	—	1.799	35.41	0.80	36.05	3.19
1.529	7.51	9.70	—	—	1.802	35.89	0.88	39.03	14.73
1.510	8.86	8.09	—	—	—	35.97	0.64	37.20	5.93
1.496	9.99	6.13	—	—	1.801	36.14	0.54	37.68	6.27
1.471	11.78	4.18	—	—	1.818	38.11	0.71	—	—
1.460	12.61	3.38	10.60	16.05	1.837	38.81	1.12	—	—
1.479	15.89	1.17	—	—	1.809	38.93	1.16	—	—
1.482	16.41	1.11	—	—	1.814	38.27	0.74	39.80	5.32
1.580	22.15	0.14	18.13	19.50	1.814	37.79	0.43	39.35	10.17
1.610	23.22	0.11	—	—	1.814	37.97	0.41	40.38	9.08
1.646	24.18	0.14	—	—	1.812	38.14	0.39	39.16	3.36
1.680	26.43	0.23	—	—	1.812	38.69	0.50	39.17	4.80
1.680	27.18	0.20	—	—	—	38.75	0.36	40.50	5.60
1.680	27.31	0.23	—	—	1.823	38.97	0.36	40.12	8.48
1.690	27.56	0.28	—	—	—	45.80	0.44	42.36	8.98
1.692	27.62	0.31	—	—	1.834	47.01	0.20	45.13	5.73
1.690	28.17	0.28	—	—	1.841	51.78	0.14	—	—
1.721	29.19	0.49	—	—	1.915	57.50	0.40	—	—
1.728	29.35	0.55	—	—	—	58.94	0.88	—	—
—	31.50	1.33	30.48	5.58	Solid phase $\text{CrO}_3\cdot\text{SO}_3$				
1.756	31.42	0.97	—	—					
1.771	31.93	1.23	—	—					
1.786	32.64	1.62	—	—					

TABLE II.

*Molecular percentages and densities at 45°.*

Liquid.			Wet solid.		Liquid.			Wet solid.	
$d_4^{45}$	$\text{SO}_3$	$\text{CrO}_3$	$\text{SO}_3$	$\text{CrO}_3$	$d_4^{45}$	$\text{SO}_3$	$\text{CrO}_3$	$\text{SO}_3$	$\text{CrO}_3$
—	5.25	13.79	4.15	34.80	33.55	1.15	36.89	13.99	—
—	16.73	1.00	9.55	37.49	34.67	1.11	38.27	14.65	—
—	22.01	0.17	14.11	34.92	35.40	1.06	41.24	15.77	—
1.751	31.05	1.16	19.35	36.62	37.07	0.63	39.88	11.52	—
—	—	—	—	—	1.797	38.10	0.60	39.62	8.24
—	—	—	—	—	1.814	42.26	0.38	44.11	9.89
—	—	—	—	—	—	45.67	0.30	44.06	3.80

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CCXXXII.—Attempts to Prepare Red Sulphide Dyes.  
Part I.

By EDWIN ROY WATSON and SIKHIBHUSHAN DUTT.

SULPHIDE dyes are known of all colours except red. On account of the fastness of this group of dyes to almost all agencies, a cheap red sulphide dye would be appreciated. The blue and black sulphide dyes are generally regarded as thiazine dyes containing mercaptan groups, and since the ordinary thiazine dyes have neither the affinity for cotton nor the fastness of sulphide dyes it is natural to attribute these properties in the latter rather to the mercaptan groups than to the thiazine chromophore. Attempts have already been made to prepare red sulphide dyes by introducing mercaptan groups into red dyes of other groups (D.R.-P. 181125; Friedländer and Mauthner, *Z. farb. Ind.*, **3**, 333; Müller, *ibid.*, **5**, 357; D.R.-P. 161462; Fichter, Fröhlich, and Jalon, *Ber.*, 1907, **40**, 4420; D.R.-P. 204772, 241985, 220628), but the results have not been very satisfactory.

It was thought that in some of these cases the dyeings were not fast because the dyes contained ordinary auxochromes, such as amino- or hydroxyl groups, as well as mercaptan groups, and the presence of these ordinary auxochromes caused the dyeings to be stripped to a certain extent by acids or alkalis. Some substances were therefore prepared containing chromophores and mercaptan groups, but no ordinary auxochromes. 4-Benzeneazo-1-naphthylmercaptan,  $C_6H_5 \cdot N_2 \cdot C_{10}H_6 \cdot SH$ , is soluble in sodium sulphide, but only dyes light brownish-yellow shades. pp'p'-Trithioltriphenylcarbinol,  $OH \cdot C(C_6H_4 \cdot SH)_3$ , is a colourless substance.

The above idea not having borne fruit, it was yet hoped that mercaptan derivatives of dyes of the various groups might prove more valuable red sulphide dyes than the compounds prepared by previous investigators (*vide supra*). The well-known influence of relative positions of chromophore and auxochromes on dyeing properties, colour, and fastness gave ground for this hope. But the various new compounds of the azine, oxazine, phthalcin, nitroso- and acridine groups which have now been prepared have all failed for one reason or another. 2-Amino-8-thiol-10-phenylphenazonium hydroxide is a sulphide dye, but gives dull violet shades; 3-amino-7-dimethylamino-4-thiolphenazine is a sulphide dye, but gives reddish-brown shades very sensitive to acids and alkalis; 9-dimethylamino-2-thiol-3-phenozone is soluble in sodium sulphide, but gives only light indigo-blue shades: dithiolfluorescein is soluble in sodium sulphide, but has no affinity for cotton from

a sulphide bath; *dinitrosothiolresorcinol* is soluble in sodium sulphide, but has no affinity for cotton; 2:8-diamino-3:7-dithiol-acridine is soluble in sodium sulphide, but only dyes light brown shades on cotton.

The *dithiolfluorescein* which we have prepared by condensation of thiolresorcinol and phthalic anhydride is perhaps identical with the thiofluorescein prepared by Maki (*J. Coll. Eng. Tokyo Imp. Univ.*, 1920, 11, i, 1) from fluorescein and sodium sulphide, although our preparation is fluorescent in alkaline solution whilst Maki's thiofluorescein is not.

The preparation and properties of some mercaptan derivatives of azo-dyes and some new compounds used as intermediates in their preparation will be described in Part II.

#### EXPERIMENTAL.

*Ethyl 4-Benzeneazo-1-naphthyl Xanthate*,  $C_6H_5 \cdot N_2 \cdot C_{10}H_7 \cdot S \cdot CS \cdot OEt$ .—Benzeneazo- $\alpha$ -naphthylamine hydrochloride (2.8 grams) was diazotised, the diazo-solution (150 c.c.) filtered from a little insoluble matter (0.25 gram), almost neutralised, and added gradually to a solution of 1.6 grams of potassium xanthate in a little water at 70°. The mixture was heated at 100° for one hour, and the oily product set to a solid on cooling (Found: S = 17.7,  $C_{19}H_{16}ON_2S_2$  requires S = 18.2 per cent.).

*4-Benzeneazo-1-naphthyl Mercaptan*,  $C_6H_5 \cdot N_2 \cdot C_{10}H_7 \cdot SH$ .—The xanthate, obtained as in the foregoing preparation, was dissolved in 500 c.c. of alcohol containing 5 c.c. of 20 per cent. aqueous sodium hydroxide and boiled for thirty minutes. After removing alcohol, water was added, and the filtered solution acidified with acetic acid, when an uncrystallisable, reddish-brown precipitate (0.35 gram) was obtained which melted below 100° (Found: S = 10.6.  $C_{16}H_{12}N_2S$  requires S = 12.1 per cent.).

This substance dissolved in aqueous sodium sulphide with a red colour and dyed cotton red, but on exposure to the air the colour changed to a light brownish-yellow shade.

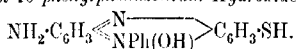
Attempts to prepare the mercaptan *via* the diazo-disulphide gave a product which was insoluble in sodium sulphide.

*pp'p'-Triithioltri-phenylcarbinol*,  $OH \cdot C(C_6H_4 \cdot SH)_3$ .—Pararosaniline (3.5 grams) was diazotised, the diazo-solution (60 c.c.) neutralised, and added gradually to a solution of 5 grams of potassium xanthate in a little water kept at 70°. The first addition was followed by a slight explosion, and further additions caused explosions of diminishing intensity. The mixture was kept at 70° for an hour after the diazo-solution had been added. The substance which separated as a yellow oil and solidified on cooling was dissolved

in ether, the ethereal solution shaken with dilute sodium hydroxide and sulphuric acid successively, the ether evaporated, and the residue boiled for half an hour with 25 c.c. of alcohol and 1.5 grams of potassium hydroxide. After evaporating off the alcohol, the residue was dissolved in water and acidified. The almost white precipitate obtained was insoluble in alcohol, benzene, or acetic acid, but soluble in sodium sulphide (Found:  $S = 24.6$ .  $C_{19}H_{16}OS_3$  requires  $S = 26.9$  per cent.).

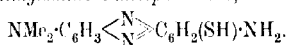
Attempts to prepare the mercaptan *via* the diazo-disulphide were not successful.

2-Amino-8-thiol-10-phenylphenazonium Hydroxide,



Phenosafranine (0.7 gram) was dissolved in 70 c.c. of water, hydrochloric acid was added in the proportion of 2 mols. (+10 per cent.) for each molecule of phenosafranine, and 2.2 c.c. of *N*-sodium nitrite solution. This diazo-solution was poured into a solution of 0.64 gram of potassium xanthate in a little water, when a dark, solid precipitate was obtained. This was boiled with water, dissolved in alcohol, giving a magenta-coloured solution, and boiled for eight hours after adding 1.5 grams of sodium hydroxide. The alcohol was evaporated off, the residue dissolved in water, and the solution acidified with hydrochloric acid. A blackish-violet precipitate was obtained which could not be crystallised. It dissolved in aqueous sodium sulphide and dyed dull violet shades on cotton (Found:  $S = 10.4$ .  $C_{18}H_{15}ON_3S$  requires  $S = 10.0$  per cent.).

3-Amino-7-dimethylamino-4-thiolphenazine,



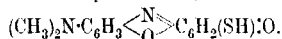
—This was prepared by the condensation of di-*m*-phenylenediamine disulphide and nitrosodimethylaniline. The former substance was prepared according to D.R.-P. 86096, but could not be obtained crystalline by the method there described. It was dissolved in acetone and poured into water. A milky emulsion was obtained, from which the substance was precipitated as fine, yellow needles by the cautious addition of a saturated solution of sodium chloride. It melted at  $65\text{--}73^\circ$  and analysis showed it to be a mixture of the disulphide with some higher sulphide or sulphides agreeing with the average formula  $C_6H_7N_2S_{1.25}$  (Found:  $S = 27.2$ . Calc.,  $S = 27.2$  per cent.).

Di-*m*-phenylenediamine disulphide (0.7 gram) was dissolved in 15 c.c. of 3.3 per cent. hydrochloric acid, nitrosodimethylaniline hydrochloride (0.94 gram), dissolved in 10 c.c. of water and 20

drops of concentrated hydrochloric acid, was added, and the mixture boiled, when a dark-coloured substance was soon deposited, which could not be crystallised. The substance is soluble in aqueous sodium sulphide with a brown colour and dyes cotton. On acidification, the dyeing has a violet shade, but is changed to reddish-brown by dilute sodium carbonate. This dyestuff was found to have the average formula which would result from the condensation of  $C_6H_7N_2S_{1.25}$  with 1 mol. of nitrosodimethylaniline (Found:  $S = 14.8, 14.5$ .  $C_{14}H_{14}N_4S_{1.25}$  requires  $S = 14.4$  per cent.).

On diazotising this substance and boiling with water, there was obtained a product which was also a sulphide dye (7-dimethylamino-3-hydroxy-4-thiophenazine?) giving dyeings which were still sensitive to acids and alkalis, but duller than those of the original dyestuff. Similar shades were obtained by diazotising on the fibre and subsequently boiling with water.

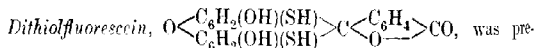
9-Dimethylamino-2-thiol-3-phenoxazone,



—This was prepared by the condensation of nitrosodimethylaniline and thiolresorcinol prepared according to D.R.-P. 41514. The amount of sulphur in the thiolresorcinol depends entirely on the amount taken in its preparation, as besides dithiolresorcinol disulphide there are formed polysulphides. The sample prepared for this purpose contained  $S = 24.8$  per cent., which corresponds with the average formula  $C_6H_3(OH)_2S_{1.13}H$ .

Nitrosodimethylaniline hydrochloride (2 grams) was almost entirely dissolved in 50 c.c. of boiling alcohol, finely powdered thiolresorcinol (0.92 gram) added, and the mixture boiled overnight. A greenish-black precipitate was obtained which was purified by extraction with carbon disulphide (to remove free sulphur) and a boiling acid solution of zinc chloride, which removed some colouring matter and finally left a substance insoluble in this reagent. It could not be crystallised (Found:  $S = 12.8$ .  $C_{14}H_{12}O_2N_2S_{1.13}$  requires  $S = 13.1$  per cent.).

This substance is soluble in aqueous sodium sulphide with a reddish-black colour, but gives only very light indigo-blue dyeings on cotton.

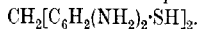


pared by heating a powdered mixture of thiolresorcinol (2.2 grams), 1 gram of phthalic anhydride, and 0.46 gram of anhydrous zinc chloride at  $150-190^\circ$  for one hour. The product was powdered, washed with water, dissolved in caustic soda, and reprecipitated with acid. It was obtained as a reddish-brown solid soluble in

caustic soda with a red colour and dark green fluorescence. It could not be crystallised (Found:  $S = 18.3$ .  $C_{20}H_{11}O_5S_{2.28}$  requires  $S = 17.9$  per cent.). (The same sample of thiolresorcinol was used as in the last preparation.) It dissolves in aqueous sodium sulphide solution with a red colour, but has scarcely any affinity for cotton.

*Dinitrosothiolresorcinol*,  $C_6HO_2(NO)_2SH$ .—Thiolresorcinol (3.4 grams) was dissolved in a little sodium hydroxide solution, 3 grams of sodium nitrite were added, the solution was cooled with ice and acidified with hydrochloric acid. A brown precipitate was obtained which was filtered off after a few hours. It is soluble in caustic soda and in sodium sulphide, but does not dye cotton from a sulphide vat (Found:  $S = 17.2$ .  $C_6H_4O_4N_2S_{1.13}$  requires  $S = 17.8$  per cent.). (This was prepared with the same sample of thiolresorcinol as was used in the preceding two preparations.)

2 : 2' : 4 : 4'-Tetra-amino-5 : 5'-dithioldiphenylmethane,



—Di-*m*-phenylenediamine disulphide (1.4 grams) was dissolved in 2 c.c. of concentrated hydrochloric acid diluted to 20 c.c. with water, and treated with 3 c.c. of 40 per cent. formaldehyde solution, when the above-mentioned compound was immediately formed as a buff-coloured precipitate (Found:  $S = 26.85$ .  $C_{13}H_{15}N_4S_{2.5}$  requires  $S = 26.1$  per cent.). (The same sample of di-*m*-phenylenediamine disulphide was used as in the preparation of the preceding phenazine dyestuff.)

This compound was made into a paste with water and boiled with ferric chloride and a few drops of hydrochloric acid, when the buff-coloured suspension soon became dark brown. The product (*diaminodithiolacridine*?) is soluble in sodium sulphide and gives light brown shades on cotton.

The substances described in this paper were first prepared in British Dyes laboratory at Leeds University and have been again prepared and analysed in the chemical laboratory at Dacca University. Our thanks are due to the British Dyestuffs Corporation, Ltd., for permission to publish these results.

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CCXXXIII.—*Dyes Derived from Phenanthraquinone.*  
*Part I. Phenanthranaphthazines.*

By ANUKUL CHANDRA SIRCAR and SIKHIBHUSAN DUTT.

UNTIL recently (Watson and Dutt, T., 1921, 119, 1211), substituted phenanthraquinone had not been condensed with *o*-phenylenediamine, and except in a few instances (Witt, Thorpe's "Dictionary of Applied Chemistry," Vol. I, p. 354; Watson and Dutt, *loc. cit.*, p. 1218) the condensation with 1:2-naphthylenediamine or its substitution products has not been described. This communication deals with the preparation and properties of the azines obtained by condensing substituted phenanthraquinone with 1:2-naphthylenediamine and its 5-sulphonic acid. The following derivatives of phenanthraquinone have been utilised: 2:7- and 4:5-dinitro-, 2- and 4-nitro-, and 2:7-dibromo-phenanthraquinones, and also dibromonitro-, bromodinitro-, and 5-bromo-4-nitro-phenanthraquinones (Mukherjee and Watson, T., 1916, 109, 623). The azines thus obtained all dye yellow shades on wool, which are very light in the case of the bromo-compounds and somewhat deeper in that of the nitro-derivatives.

As these azines did not contain auxochromic groups, phenanthranaphthazines were prepared by the condensation of 1:2-naphthylenediamine with 2:7-diamino-, 4:5-diamino-, 2-amino-, 4-amino-, 2:7-dihydroxy-, 4:5-dihydroxy-, 2-hydroxy-, and 4-hydroxy-phenanthraquinones. Although insoluble in water, the azines thus obtained are moderately soluble in some of the common organic solvents, and their tinctorial properties are on the whole satisfactory. They dye wool from an acid bath in shades varying from bright yellow to dark brown; 4:5-dihydroxyphenanthranaphthazine dyes chrome-mordanted wool to a deep brown shade.

In attempting to prepare 2:7-diaminophenanthranaphthazine by the reduction of the corresponding dinitro-compound with tin and hydrochloric acid, instead of the desired substance, 2:7-diaminodihydrophenanthranaphthazine was formed. The amino-groups in the diaminodihydro-compound were easily replaced by hydroxy-groups by the diazo-reaction, and 2:7-dihydroxydihydrophenanthranaphthazine obtained. The dyeing properties of these dihydro-derivatives are not satisfactory (compare Watson and Dutt, *loc. cit.*, p. 1213).

In the anthraquinone series, bromine atoms are easily replaced by anilino-groups by Ullmann's method (*Ber.*, 1901, 34, 2174). Mukherjee and Watson have shown that Ullmann's reaction can also be applied in the phenanthraquinone series. These anilino-

derivatives in many cases possess interesting dyeing properties. Further, from an examination of the constitutional formulæ of the commercial azine dyes, it is found that the anilino-compounds, for example, indamine-blue, generally dye blue shades, whilst the corresponding azines without the anilino-groups dye redder shades. Led by these considerations, the authors applied Ullmann's method to the bromophenanthranaphthazines and found that these substances can be readily converted into the corresponding anilino-compounds. 2:7-Dianilino-, 4-nitro-5-anilino-, dinitroanilino-, and nitrodianilino-phenanthranaphthazines have been prepared in this way. They dye full shades on wool in colours ranging from olive-green to bluish-green or bottle-green. They are insoluble in water and only sparingly soluble in the ordinary organic solvents.

The azines mentioned so far are all insoluble in water; many of them are almost insoluble in the ordinary organic solvents and can be crystallised only from liquids of high boiling point. The introduction of sulphonic acid groups into the molecules of these azines should tend to make them soluble in water, and possibly such sulphonic acid derivatives could be crystallised from this solvent. 1:2-Naphthylendiamine-5-sulphonic acid was therefore condensed with 2:7-diamino-, 2-amino-, and 2:7-dihydroxy-phenanthraquinone. The sodium salts of the azines thus obtained are all soluble in water and dye wool in brown to maroon shades from an alkaline bath. The dyeings thus obtained are much deeper in shade than those of the corresponding unsulphonated compounds. Evidently the sulphonic acid group has a marked influence in deepening the colours of the original compounds—this, however, is not generally the case.

The phenanthranaphthazines described in this paper (1) are characterised by their high melting points (many of them decompose before melting), their sparing solubility in the ordinary organic solvents, their well-developed tinctorial properties, and their stability towards oxidising agents; (2) dissolve in concentrated sulphuric acid with characteristic colour; water precipitates them unchanged as light, flocculent masses, particularly adapted for dyeing purposes.

#### EXPERIMENTAL.

2:7-Dinitrophenanthranaphthazine,  $(\text{NO}_2)_2\text{C}_{14}\text{H}_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_{10}\text{H}_6$ —

The crystalline precipitate produced by boiling 2.9 grams of 2:7-dinitrophenanthraquinone and 1.6 grams of 1:2-naphthylendiamine in 400 c.c. of glacial acetic acid, separated from amyl alcohol in yellow needles not melting below 290°. It is sparingly soluble in alcohol, acetone, acetic acid, chloroform, or benzene, moderately



soluble in aniline or amyl alcohol, and very soluble in pyridine or nitrobenzene. It dissolves in strong sulphuric acid with a violet colour, and when reprecipitated by water dyes wool light-yellow shades from an acid bath (Found: N = 13.32.  $C_{24}H_{22}O_4N_4$  requires N = 13.33 per cent.).

**4:5-Dinitrophenanthranaphthazine.**—The crystalline precipitate obtained by mixing 2.9 grams of 4:5-dinitrophenanthraquinone and 1.6 grams of 1:2-naphthylenediamine in 200 c.c. of boiling acetic acid, recrystallised from nitrobenzene in yellow needles melting at 275°. Its properties resemble those of the preceding compound (Found: N = 13.38 per cent.).

**2-Nitrophenanthranaphthazine,**  $NO_2 \cdot C_{14}H_7 \llbracket \begin{smallmatrix} N \\ N \end{smallmatrix} \rrbracket C_{10}H_6$ , was obtained in the same way as the preceding compound by condensing 2-nitrophenanthraquinone with 1:2-naphthylenediamine. It crystallised from aniline in yellow needles melting at about 190° (with decomposition) (Found: N = 11.41.  $C_{24}H_{13}O_2N_3$  requires N = 11.2 per cent.).

**4-Nitrophenanthranaphthazine** was prepared from 4-nitrophenanthraquinone in the same way as the preceding compounds and obtained as yellow needles (from acetic acid), melting at 206–208° (Found: N = 11.63 per cent.).

The properties of the two mononitro-azines resemble those of the dinitro-compounds described above.

**2:7-Diaminophenanthranaphthazine,**  $(NH_2)_2C_{14}H_6 \llbracket \begin{smallmatrix} N \\ N \end{smallmatrix} \rrbracket C_{10}H_5$ ,—The precipitate produced by boiling 1.15 grams of 2:7-diaminophenanthraquinone and 0.8 gram of 1:2-naphthylenediamine in 30 c.c. of glacial acetic acid for one hour, separated in yellow needles from hot pyridine on cautious addition of hot water.

It decomposes on heating and is sparingly soluble in acetic acid, alcohol, acetone, benzene, or chloroform and readily soluble in nitrobenzene, pyridine, or aniline. It dyes bright yellow shades on wool from an acid bath (Found: N = 15.34.  $C_{24}H_{16}N_4$  requires N = 15.56 per cent.).

**4:5-Diaminophenanthranaphthazine** was prepared in a similar way to the preceding compound, and crystallised from pyridine as yellow needles, decomposing at about 170° (Found: N = 15.81 per cent.).

**2-Aminophenanthranaphthazine,**  $NH_2 \cdot C_{14}H_7 \llbracket \begin{smallmatrix} N \\ N \end{smallmatrix} \rrbracket C_{10}H_5$ ,—2-Aminophenanthraquinone (1.5 grams) and 1:2-naphthylenediamine (1.1 grams) were boiled for three hours in 20 c.c. of absolute alcohol. The colour of the aminoquinone rapidly changed to

yellow and a crystalline precipitate separated. This crystallised from pyridine as yellow, prismatic needles, melting at  $250^{\circ}$  (Found:  $N = 12.68$ .  $C_{24}H_{15}N_3$  requires  $N = 12.2$  per cent.).

4-Aminophenanthranaphthazine, prepared in a similar way to the preceding compound, melts at  $180-181^{\circ}$  (Found:  $N = 12.2$  per cent.).

The properties of the mono-aminophenanthranaphthazines resemble those of the diamino-compounds.

2:7-Dihydroxyphenanthranaphthazine,  $(OH)_2C_{14}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_{10}H_6$ .

—The crystalline mass produced by boiling molecular quantities of 2:7-dihydroxyphenanthraquinone and 1:2-naphthylenediamine in the minimum quantity of acetic acid, separated from the same solvent as yellowish-brown needles melting at  $220-221^{\circ}$ . It dissolves in potassium hydroxide solution with a brown colour and dyes wool brown shades from an acid bath (Found:  $N = 7.66$ .  $C_{24}H_{14}O_2N_2$  requires  $N = 7.74$  per cent.).

4:5-Dihydroxyphenanthranaphthazine, prepared in a similar way to the preceding compound, separated from dilute acetic acid in orange-brown, prismatic needles, decomposing at  $175^{\circ}$  (Found:  $N = 8.05$  per cent.).

2-Hydroxyphenanthranaphthazine,  $OH \cdot C_{14}H_7 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_{10}H_6$ .—The

brown needles produced by boiling molecular quantities of 2-hydroxyphenanthraquinone and 1:2-naphthylenediamine for ten minutes in acetic acid, were recrystallised from dilute acetic acid. The substance decomposes above  $160^{\circ}$ . It dyes wool yellow shades from an acid bath and brown shades from an alkaline bath containing 3 per cent. of sodium carbonate (Found:  $N = 7.89$ .  $C_{24}H_{14}ON_2$  requires  $N = 8.09$  per cent.).

4-Hydroxyphenanthranaphthazine was obtained as brownish-yellow, prismatic needles in a similar way to the preceding compound. It begins to decompose at  $208^{\circ}$  and finally melts (with decomposition) at  $225^{\circ}$  (Found:  $N = 8.4$  per cent.).

The solubility in organic solvents of the four hydroxyphenanthranaphthazines resembles that of the amino-azines described above.

2:7-Dibromophenanthranaphthazine,  $C_{14}H_6Br_2 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} C_{10}H_6$ .—The precipitate produced by boiling equimolecular quantities of 2:7-dibromophenanthraquinone and 1:2-naphthylenediamine in acetic acid for fifteen minutes, after being washed with water, separated from nitrobenzene as light yellow needles, not melting below  $290^{\circ}$ . It is almost insoluble in ordinary organic solvents, although slightly soluble in nitrobenzene, pyridine, or aniline. It dissolves in con-

concentrated sulphuric acid with a brilliant blue colour and dyes wool light yellow shades from an acid bath (Found: Br = 33.3.  $C_{24}H_{12}N_2Br_2$  requires Br = 32.79 per cent.).

2 : 7-Dianilinophenanthranaphthazine,  $(NHPh)_2C_{14}H_6 \llcorner \begin{smallmatrix} N \\ N \end{smallmatrix} \gg C_{10}H_6$ .

—One gram of the above dibromo-compound was boiled with 10 grams of aniline and 0.3 gram of copper powder for three hours, and the hot liquid filtered into dilute hydrochloric acid. The dark green mass obtained, after being washed several times with hot dilute hydrochloric acid and water, separated from pyridine, on cautious addition of hot water, in needle-shaped, crystalline aggregates melting at  $200^\circ$ . The substance is slightly soluble in alcohol, and moderately soluble in nitrobenzene or pyridine. It dissolves in concentrated sulphuric acid with a green colour and dyes wool in olive-green shades (Found: N = 10.76.  $C_{36}H_{24}N_4$  requires N = 10.94 per cent.).

Dibromonitrophenanthranaphthazine was obtained as brownish-yellow needles by boiling 2 grams of dibromonitrophenanthraquinone, prepared by Mukherjee and Watson's method (*loc. cit.*, p. 623), and 0.8 gram of 1 : 2-naphthylenediamine in 150 c.c. of acetic acid for half an hour. It decomposes at  $235^\circ$  and is only slightly soluble in alcohol, but is very soluble in aniline, nitrobenzene, or pyridine. It dyes light yellow shades on wool from an acid bath (Found: Br = 30.00.  $C_{24}H_{11}O_2N_3Br_2$  requires Br = 30.02 per cent.).

Nitrodianilinophenanthranaphthazine was produced by submitting 1 gram of the preceding compound to Ullmann's reaction in the usual way. It could not be crystallised and was purified by boiling with dilute hydrochloric acid, dissolving in pyridine, precipitating with hot water, and finally washing with acetic acid, alcohol, and water, and obtained as a bluish-black powder melting at about  $172^\circ$  (with decomposition).

Its solubility is similar to that of the preceding compound. It dyes wool in brownish-violet shades from an acid bath (Found: N = 12.97.  $C_{36}H_{23}O_2N_5$  requires N = 12.56 per cent.).

Bromodinitrophenanthranaphthazine separated as greenish-yellow, prismatic needles on bringing together 1.19 grams of the bromodinitroquinone (Mukherjee and Watson, *loc. cit.*) and 0.8 gram of the diamine in 200 c.c. of boiling acetic acid, and was purified by recrystallisation from nitrobenzene. It does not melt below  $290^\circ$ , and in other properties resembles the dibromonitro-compound described above (Found: Br = 16.2.  $C_{24}H_{11}O_4N_4$  requires Br = 16.03 per cent.).

Dianitroanilinophenanthranaphthazine.—The black mass produced

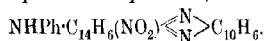
by submitting the preceding compound to Ullmann's reaction in the usual way was dissolved in pyridine and the azine separated, in black, crystalline aggregates, by the careful addition of hot water.

It decomposes on heating, and when freshly precipitated from sulphuric acid dyes wool a beautiful bottle-green shade. Its other properties are similar to those of the nitrodianilino-azine described above (Found: N = 14.19.  $C_{30}H_{17}O_4N_6$  requires N = 13.69 per cent.).

5-Bromo-4-nitrophenanthranaphthazine,  $NO_2 \cdot C_{14}H_6Br \ll N \gg C_{10}H_6$ .

—Molecular quantities of 1:2-naphthylenediamine and 5-bromo-4-nitrophenanthraquinone (m. p. 224–226°; Mukherjee and Watson, *loc. cit.*)\* were heated together in acetic acid solution. On concentrating the solution, the azine crystallised out spontaneously in shining, brown needles. It was recrystallised from a mixture of alcohol (1 part) and acetic acid (2 parts). It melts at 260°, and resembles the two bromonitro-azines described above (Found: Br = 18.04.  $C_{24}H_{12}O_2N_2Br$  requires Br = 17.62 per cent.).

4-Nitro-5-anilino-phenanthranaphthazine,



—This compound was prepared from the preceding substance in a similar way, and has similar properties, to the anilino-azines described above. It separated as bluish-black needles, melting at about 170° (with decomposition). It dissolves in strong sulphuric acid with a violet-black colour and dyes wool in bluish-green shades from an acid bath (Found: N = 12.53.  $C_{30}H_{18}O_2N_4$  requires N = 12.01 per cent.).

2:7-Diaminophenanthranaphthazine-12-sulphonic Acid,



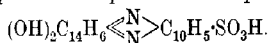
—2:7-Diaminophenanthraquinone (1 gram) and 1:2-naphthylenediamine-5-sulphonic acid (1 gram) were boiled together with a small quantity of water. The dark colour of the amino-quinone rapidly disappeared and a greenish-yellow, crystalline mass was produced. This was filtered, dissolved in dilute caustic soda solution, and again filtered. The filtrate, on acidification with dilute hydrochloric acid, deposited greenish-yellow needles, which were filtered, washed with water, and dried in a vacuum desiccator, where the colour changed to brown.

The substance is slightly soluble in alcohol or acetic acid and

\* In the original description (T., 1916, 109, 623), the position of the bromine atom is not indicated. Dr. Watson, in a private communication to one of us, states that the bromine atom occupies the 5-position.

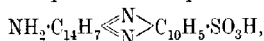
very soluble in pyridine (Found: N = 13.00.  $C_{24}H_{16}O_3N_4S$  requires N = 12.74 per cent.). With concentrated hydrochloric acid, it forms a red salt decomposable by water. The sodium salt is very soluble in water. It dyes brown shades on wool from an alkaline bath containing 2 per cent. of sodium carbonate.

2 : 7-Dihydroxyphenanthranaphthazine-12-sulphonic Acid,



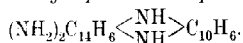
—The mass produced by boiling 2 : 7-dihydroxyphenanthraquinone (1 gram) and 1 : 2-naphthylenediamine-5-sulphonic acid with water for two hours was repeatedly extracted with hot sodium carbonate solution. The combined extracts, after concentration to a small volume, deposited, on acidification with hydrochloric acid, dark brown needles, which dyed wool a pleasant brown shade from an alkaline bath containing 2 per cent. of sodium carbonate (Found: N = 5.96.  $C_{24}H_{14}O_3N_2S$  requires N = 6.11 per cent.).

2-Aminophenanthranaphthazine-12-sulphonic Acid,



was obtained as brown needles by boiling 1.1 grams of the 2-aminoquinone and 1.2 grams of the diaminesulphonic acid with a little water for half an hour, and then adopting the same procedure as in the preparation of the 2 : 7-diamino-compound (*vide supra*). Its properties are exactly similar to those of the diamino-compound. The sodium salt is only moderately soluble in water (Found: N = 9.48.  $C_{24}H_{15}O_3N_3S$  requires N = 9.98 per cent.).

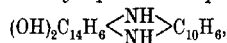
2 : 7-Diamino-9 : 16-dihydrophenanthranaphthazine,



—Two grams of 2 : 7-dinitrophenanthranaphthazine and 4 grams of tin were heated on the water-bath with 30 c.c. of fuming hydrochloric acid until the whole of the tin had dissolved. Having been washed with hydrochloric acid, the product was dissolved in water, the solution made strongly alkaline with sodium carbonate, and evaporated to dryness. The dried mass was repeatedly extracted with pyridine, from which, on cautious addition of hot water, the reduction product separated as bright yellow needles melting at 250° (with decomposition).

The solubility of the dihydro-azine in organic solvents is similar to that of 2 : 7-diaminophenanthranaphthazine, but the reduction product dissolves in concentrated sulphuric acid with a brilliant pink colour, whereas the 2 : 7-diamino-azine does so with a violet colour. This property and a determination of the melting point of the mixture established the difference between the two compounds.

2 : 7-Dihydroxy-9 : 16-dihydrophenanthranaphthazine,



was obtained as brown flocks by diazotising the preceding compound in the usual way and boiling the filtrate for some time. It was further purified by dissolving in caustic soda solution, from which hydrochloric acid precipitated a dark violet substance, not melting below 280°. It dissolves in concentrated sulphuric acid and in caustic soda solution with a violet and a brownish-violet colour, respectively.

We take this opportunity to express our thanks to Dr. E. R. Watson, who suggested the investigation and under whose supervision the preliminary work was carried out.

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#### CCXXXIV.--*Dyes Derived from Phenanthraquinone.* *Part II. Naphthaflavindulines.*

By SIKHIBHUSHAN DUTT.

IN view of the unexpected dyeing properties of the phenanthra-phenazines and -naphthazines previously described (Watson and Dutt, T., 1921, 119, 1211; Sircar and Dutt, this vol., p. 1944), it was considered desirable to prepare certain naphthaflavindulines and to examine their behaviour on the fibre. In the azine series, the chromophoric property of the azine ring appears to be enhanced by the change of a nitrogen atom from the tervalent to the quinquevalent state, that is, by the conversion of the azine to an azonium compound, as, for example, in the case of the yellow diamino-phenazine,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}\cdot\text{C}_6\text{H}_3\cdot\text{NH}_2$ , and the scarlet-red safranin,

$\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N}^+\text{PhCl} \end{smallmatrix}\cdot\text{C}_6\text{H}_3\cdot\text{NH}_2$ . It seemed probable, therefore, that azines derived from phenanthraquinone would be excelled in colour by the corresponding azonium derivatives.

The simplest naphthaflavinduline was prepared by Witt (Ber., 1887, 20, 1183), who obtained it by condensing phenanthraquinone with phenyl-1-amino- $\beta$ -naphthylamine in presence of glacial acetic and nitric acids. The dyeing properties of this compound are of

little interest, probably on account of a lack of auxochromic groups in the molecule, and therefore the following naphthaflavindulines, containing various auxochromic and other groups, have been prepared in the hope that they would have much better dyeing properties: 2:7-Dibromo-, 2:7-dianilino-, 3-bromo-, 3-anilino-, 2:7-dinitro-, 4:5-dinitro-, 2-nitro-, 4-nitro-, 2:7-diamino-, 4:5-diamino-, 2-amino-, 4-amino-, 2:7-dihydroxy-, 4:5-dihydroxy-, 2-hydroxy-, 4-hydroxy-, dibromonitro-, and bromodinitro-naphthaflavindulines.

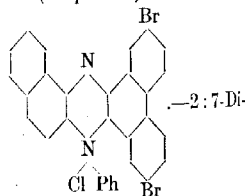
The naphthaflavindulines are, in general, dark brown to blue-black substances which crystallise with difficulty. Most of them decompose on heating and refuse to burn completely in air. They are also decomposed with difficulty by fuming nitric acid under pressure. They dissolve in concentrated sulphuric acid mostly with a brown colour and therefore, unlike the corresponding azines, do not yield characteristic colour reactions with this reagent. When freshly precipitated, they dye wool evenly from an acid bath. The dyeing properties are, on the whole, much better than those of the corresponding phenanthranaphthazines.

#### EXPERIMENTAL.

*Phenyl-1-amino- $\beta$ -naphthylamine.* — The following preparation, giving directly a 90 per cent. yield of free base, was used in preference to Witt's method, which furnishes a poor yield of hydrochloride (*Ber.*, 1887, 20, 571, 1183).

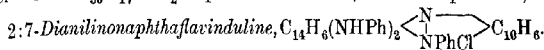
Diazobenzenesulphonic acid, obtained from sulphanilic acid (20 grams) and freed as far as possible from adherent moisture, was stirred into 22 grams of phenyl- $\beta$ -naphthylamine in 60 c.c. of glacial acetic acid at 55°, the dye, which was precipitated quantitatively, being collected after five minutes. This azo-dye was dissolved in 10 per cent. aqueous sodium hydroxide, and the filtered solution boiled with zinc dust until colourless. The residue obtained on cooling was washed with water and extracted with hot pyridine. The extract, on dilution with hot water, deposited the base in white, silky needles (m. p. 138°).

2:7-Dibromonaphthaflavinduline,



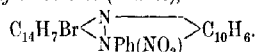
bromophenanthraquinone (1.2 grams) and 0.8 gram of phenyl-

1-amino- $\beta$ -naphthylamine, dissolved in hot glacial acetic acid, were treated with 5 c.c. of strong hydrochloric acid. The condensation product at once crystallised out in blue, microscopic needles. The compound decomposes above  $230^{\circ}$ , and is sparingly soluble in most organic solvents. When freshly precipitated from sulphuric acid solution, it dyes fine maroon shades on wool (Found: Br = 26.2; Cl = 5.9.  $C_{30}H_{17}ClBr_2$  requires Br = 26.62; Cl = 5.99 per cent.).



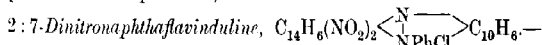
—The preceding compound (0.5 gram) was converted by Ullmann's reaction with aniline and copper powder to a bright blue, amorphous product, which could not be crystallised, but was purified by dissolving in pyridine, precipitating with alcohol, and boiling with strong hydrochloric acid. The compound, which does not melt below  $290^{\circ}$ , is sparingly soluble in the ordinary organic solvents, but dissolves fairly easily in nitrobenzene, aniline, or pyridine. When freshly precipitated, it dyes beautiful blue shades on wool (Found: N = 8.25.  $C_{42}H_{23}N_4Cl$  requires N = 8.96 per cent.).

3-Bromonaphthaflavinduline (Nitrate),



—3-Bromophenanthraquinone (2.8 grams) and 2.4 grams of phenyl-1-amino- $\beta$ -naphthylamine in cold glacial acetic acid solution were treated with 7 c.c. of concentrated nitric acid. The solution, on keeping for twenty-four hours, deposited the condensation product in orange-red needles, m. p.  $230^{\circ}$  after recrystallisation from dilute acetic acid. It is fairly soluble in alcohol or acetic acid, and very soluble in aniline, nitrobenzene, or pyridine. It dyes orange shades on wool (Found: Br = 14.2.  $C_{30}H_{18}O_3N_3Br$  requires Br = 14.6 per cent.).

3-Anilinonaphthaflavinduline (Nitrate) was prepared from the preceding compound by Ullmann's method. The green, amorphous product was purified by repeated precipitation from pyridine solution by hot water and afterwards from strong nitric acid by cold water. The substance melts and decomposes at  $195^{\circ}$  and dyes fine olive-green shades on wool (Found: N = 10.2.  $C_{36}H_{24}O_3N_4$  requires N = 10.0 per cent.).



2:7-Dinitrophenanthraquinone (2.9 grams) and 2.4 grams of phenyl-1-amino- $\beta$ -naphthylamine were condensed together in the usual manner in presence of glacial acetic and concentrated hydrochloric acids. The product was recrystallised from dilute acetic



acid in fine brown needles melting at  $220^{\circ}$  with decomposition. It dyes yellowish-grey shades on wool (Found:  $N = 10.9$ ,  $C_{30}H_{17}O_4N_3Cl$  requires  $N = 10.5$  per cent.).

4:5-Dinitronaphthaflavinduline, prepared from 4:5-dinitrophenanthraquinone, crystallises from alcohol in brown, microscopic needles, which melt with decomposition at  $190^{\circ}$ , and dyes brownish-grey shades on wool (Found:  $N = 10.43$ ,  $C_{30}H_{17}O_4NCl$  requires  $N = 10.5$  per cent.).

2-Nitronaphthaflavinduline, prepared from 2-nitrophenanthraquinone, crystallises from amyl alcohol in brown needles which decompose on heating. It yields fine terra-cotta shades on wool (Found:  $N = 8.5$ ,  $C_{30}H_{18}O_2N_3Cl$  requires  $N = 8.61$  per cent.).

4-Nitronaphthaflavinduline, prepared from 4-nitrophenanthraquinone, crystallises from amyl alcohol in dark brown needles, which melt and decompose at  $165^{\circ}$ . It yields maroon shades on wool (Found:  $N = 8.55$ ,  $C_{30}H_{18}O_2N_3Cl$  requires  $N = 8.61$  per cent.).

2:7-Diaminonaphthaflavinduline.—Two grams of 2:7-diaminophenanthraquinone, dissolved in 150 c.c. of hot glacial acetic acid containing 30 c.c. of nitrobenzene, were treated with 2 grams of phenyl-1-amino- $\beta$ -naphthylamine, and through the solution a current of dry hydrogen chloride was passed. The condensation product crystallised in fine, dark blue, microscopic needles, which decomposed on heating. The compound is slightly soluble in acidified water, and dyes wool to a beautiful bluish-black shade (Found:  $N = 11.62$ ,  $C_{30}H_{21}N_4Cl$  requires  $N = 11.84$  per cent.).

4:5-Diaminonaphthaflavinduline was obtained from 4:5-diaminophenanthraquinone. It melts and decomposes above  $290^{\circ}$  and yields violet-black shades on wool (Found:  $N = 11.71$ ,  $C_{30}H_{21}N_4Cl$  requires  $N = 11.84$  per cent.).

2-Aminonaphthaflavinduline.—2-Aminophenanthraquinone hydrochloride (1.2 grams) and 1.4 grams of phenyl-1-amino- $\beta$ -naphthylamine hydrochloride were mixed in hot glacial acetic acid solution. On cooling, the condensation product crystallised in fine, blue, microscopic needles. The substance melts and decomposes at  $195^{\circ}$  and yields dull bluish-black shades on wool (Found:  $N = 9.17$ ,  $C_{30}H_{20}N_3Cl$  requires  $N = 9.1$  per cent.).

4-Aminonaphthaflavinduline was obtained from 4-aminophenanthraquinone in a manner similar to the above. The substance, which crystallises in blue needles, melts with decomposition at  $128-130^{\circ}$ , and dyes dull violet-blue shades on wool (Found:  $N = 8.82$ ,  $C_{30}H_{20}N_3Cl$  requires  $N = 9.1$  per cent.).

2:7-Dihydroxynaphthaflavinduline.—Two grams of 2:7-dihydroxyphenanthraquinone and 2 grams of phenyl-1-amino-

$\beta$ -naphthylamine were condensed together in the usual manner in presence of glacial acetic and concentrated hydrochloric acids. The product gradually crystallised in brown needles, m. p.  $245^{\circ}$  (decomp.). The substance is slightly soluble in water and dissolves in alkalis with a dark brown colour. It yields fine Vandyke-brown shades on wool (Found: N = 5.95.  $C_{30}H_{19}O_2N_2Cl$  requires N = 5.9 per cent.).

4 : 5-Dihydroxynaphthaflavinduline, obtained from 4 : 5-dihydroxyphenanthraquinone, crystallises from dilute acetic acid in dark brown needles, not melting below  $290^{\circ}$ . It dissolves in alkalis with a yellowish-brown colour and dyes fine nut-brown shades on wool (Found: N = 5.54.  $C_{30}H_{19}O_2N_2Cl$  requires N = 5.9 per cent.).

2-Hydroxynaphthaflavinduline was obtained from 2-hydroxyphenanthraquinone in a similar way to the 2 : 7-dihydroxy-compound. It crystallises from a mixture of amyl and ethyl alcohols in microscopic, bluish-brown needles, m. p.  $174^{\circ}$  (decomp.). It is very slightly soluble in water and dissolves in alkalis with a dirty brown colour. It yields clay-coloured shades on wool (Found: N = 5.8.  $C_{30}H_{19}ON_2Cl$  requires N = 6.1 per cent.).

4-Hydroxynaphthaflavinduline, obtained from 4-hydroxyphenanthraquinone, crystallises from dilute acetic acid in dark brown, microscopic needles, which melt and decompose at  $192^{\circ}$ . It is slightly soluble in water and dissolves in alkalis with a yellowish-brown colour. It dyes flesh-coloured shades on wool (Found: N = 5.6.  $C_{30}H_{19}ON_2Cl$  requires N = 6.1 per cent.).

*Dibromonitronaphthaflavinduline*.—Dibromonitrophenanthraquinone (Mukherjee and Watson, T., 1916, **109**, 617) (1.9 grams) and 1.1 grams of phenyl-1-amino- $\beta$ -naphthylamine were digested in concentrated sulphuric acid (20 c.c.) for ten minutes at the ordinary temperature, and the solution was poured into water. The precipitate was collected, boiled with concentrated hydrochloric acid for some time, and crystallised from glacial acetic acid. The substance, obtained in fine, dark brown needles, melts and decomposes at  $230^{\circ}$ , and yields beautiful sepia shades on wool (Found: Br = 25.1.  $C_{30}H_{16}O_2N_3ClBr_2$  requires Br = 24.8 per cent.).

*Bromodinitronaphthaflavinduline* was prepared from bromodinitrophenanthraquinone (Mukherjee and Watson, *loc. cit.*) in a similar way to the above. It crystallises from glacial acetic acid in brown, microscopic needles, which melt and decompose at  $205$ – $207^{\circ}$ , and yields brown shades on wool (Found: Br = 13.2.  $C_{30}H_{16}O_4N_3ClBr$  requires Br = 13.09 per cent.).

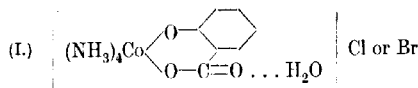
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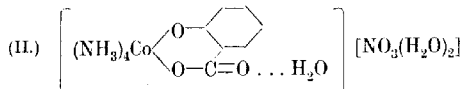
CCXXXV.—*Researches on Residual Affinity and Co-ordination. Part X. Salicylatotetramminocobaltic Salts and the Constitution of Oxonium Compounds.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN an investigation of the cobaltammine lakes of azo-dyes derived from salicylic acid, it became desirable to prepare the pentamminocobaltic salt of salicylic acid itself, and this lake was obtained as a sage-green, insoluble precipitate, but in attempting to vary the method of production by adding dry salicylic acid to a warm solution of cobaltammine reagent (this vol., pp. 165 and 1969), we found that an intermediate product was formed which separated in well-defined, dark red crystals. This compound proved to be *salicylatotetramminocobaltic chloride* (formula I) containing a new cobaltammine complex in which the bivalent salicylate radicle is implicated as a chelate group.



By employing a cobaltammine reagent containing bromine, the corresponding bromide was produced with equal readiness. Both compounds contained one molecular proportion of water, which was not evolved below 135°. The reaction was then extended to the production of other members of the series, and it was found that the normal salts of the new complex with various acids contained at least one molecule of water, which was tenaciously retained. The *nitrate* (II), for example, crystallised with 3H<sub>2</sub>O, but two were evolved at 100°.



The *iodide* and *iodate* each contained 3H<sub>2</sub>O and the *sulphate* 4H<sub>2</sub>O, but only one molecule of water per complex was retained above 100°.

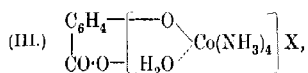
1. *The Salicylatotetramminocobaltic Complex as a Compound Alkali Ion.*

The new univalent salicylatotetramminocobaltic complex has the singular property of simulating the behaviour of the sodium ion in regard to the solubility of its salts in water. Acidic radicles which serve as precipitants for the sodium ion give rise to sparingly

soluble salicylatotetramminocobaltic salts. The *oxalate* and *α-naphthylamine-S-sulphonate* are sparingly soluble. The *bicarbonate* (VIII) is much less soluble than the *carbonate* (p. 1967), and the *hydrogen silicofluoride* (X) is also sparingly soluble. The chloride, bromide, and iodide of the salicylato-complex have the same order of solubility as sodium chloride, bromide, and iodide. Moreover, the new complex iodide and iodate both separate with two loosely attached molecules of water, thus resembling dihydrated sodium iodide and iodate.

## 2. The Salicylatotetramminocobaltic Radicle as an Oxonium Complex.

The constant occurrence of firmly held water in the normal salts of the new series raises the question of the chemical constitution of the salicylato-complex. It seemed possible at first that the water molecule was directly associated with the central cobalt atom as in the acidoaquotetramminocobaltic salts,  $\left[ \begin{smallmatrix} \text{Cl} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_2$  (Vortmann, *Ber.*, 1877, **10**, 1451; Werner and Wolberg, *ibid.*, 1905, **38**, 2009), where only one co-ordination position is left for the implicated acido-radicle. A description of the new salicylato-salts on this basis would lead to the following formula,

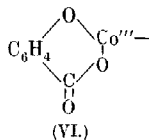
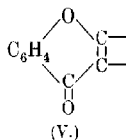
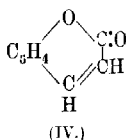


which indicates only one limb of the chelate group as implicated in the co-ordination sphere, the other and probably the carboxo-, CO-O-limb being present in the form of a "bound" ion.\* In the present instance, however, another explanation is much more probable, namely, that this firmly held water is co-ordinated, not with cobalt, but with the unsaturated carbonyl oxygen. This leaves two co-ordination positions round cobalt which are filled by the bivalent salicylate radicle functioning as a chelate group. This configuration, which is symbolised in formulae I and II, is supported by the following considerations.

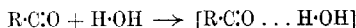
\* The hypothesis of the "bound" ion finds abundant experimental justification in our earlier communications on the cobaltamine lakes of mordant dyes (T., 1921, **119**, 704; 1922, *loc. cit.*), in which sulphonate ions are bound up in complex molecules of the lakes, this tying up of the ions being often accompanied by very appreciable decrease in the solubility of the lake. Pfeiffer has now made use of this conception in a new theory of the constitution of the betaines (*Ber.*, 1922, **55**, [B], 1764) . . . "Der ganze Unterschied im Aufbau des Kochsalzes oder Natriumacetats einerseits und der Betaine andererseits besteht also darin, dass in den ersteren Salzen die Ionen getrennt nebeneinander liegen, während in den Betainen die Ionen durch Atomketten miteinander verknüpft sind."

The presence of the firmly held water molecule in the salicylato-series of normal cobaltammine salts is reminiscent of the oxonium salts of coumarin (Morgan and Micklethwait, T., 1906, **89**, 863), in which it was shown that each molecule of this aromatic lactone is accompanied by one molecule of water:  $(C_9H_6O_2 \cdot H_2O)_4 H_2PtCl_6$ ,  $(C_9H_6O_2 \cdot H_2O)_4 HAnCl_4$ , and  $(C_9H_6O_2 \cdot H_2O)_3 H_3Co(CN)_6$ .

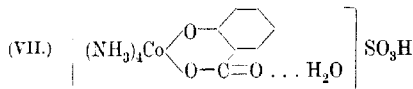
It will be noticed that the salicylato-complex has a skeletal structure (VI) containing oxygen atoms in a state of combination similar to that in which this element exists in the  $\alpha$ - and  $\gamma$ -pyrones (IV and V).



This analogy in chemical structure leads to a similar tendency towards the formation of hydrates in which the electronegative oxygen of the unsaturated carbonyl group becomes associated co-ordinatively with the electropositive hydrogen of water.

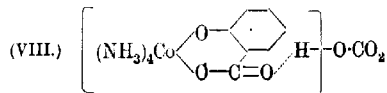


If this view of the position of the water molecules in the salicylato-series of salts is correct, it should be possible to replace this water by other compounds containing electropositive hydrogen. This anticipation has been confirmed by a study of the acid salts (hydrogen salts) of the new series. Our experimental results show that the firmly held water molecule is absent from these acid salts. This elimination of water has been shown to be general with the significant exception of the *bisulphite* (VII), and it is a fair inference

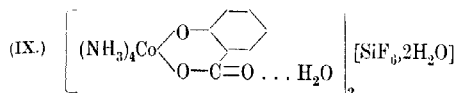


that the positive hydrogen of the acid salt has replaced the water molecule in the oxonium complex. This replacement of water of hydration by positive hydrogen takes place with acids of varying basicity and widely different strengths.

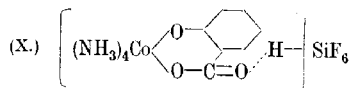
*Salicylatotetramminocobaltic bicarbonate* (VIII), a well-defined hydrogen salt and a key to the preparation of other compounds of the series, is anhydrous.



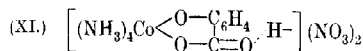
By double decomposition from the bicarbonate, hydrofluosilicic acid furnishes two salts, the normal *salicylatotetramminocobaltic silicofluoride* (IX), with two firmly attached water molecules, and



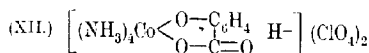
the acid or *hydrogen silicofluoride* (X), which is anhydrous.



It is significant in this connexion that the monobasic acids such as nitric and perchloric acids which give stable oxonium salts (Kehrmann and Mattison, *Ber.*, 1902, **35**, 343; K. A. Hofmann, Metzler, and Lecker, *Ber.*, 1910, **43**, 178) also furnish anhydrous hydrogen salts with the salicylato-complex. The *hydrogen dinitrate* (XI) is free from co-ordinated water and stable in air, differing entirely in this respect from the hydrated, hygroscopic, normal nitrate (II).



*Salicylatotetramminocobaltic hydrogen diperchlorate* (XII), also obtained from the bicarbonate, is a similarly constituted anhydrous salt.



### 3. Observations on the Theory of Oxonium Salts.

The older theory of oxonium salts was based on the view that under certain conditions bivalent oxygen could become quadrivalent by entering into direct combination with the electropositive and electronegative ions of an acid to form a salt analogous in constitution to ammonium salts when the latter were regarded as being derived from quinquivalent nitrogen. The current electronic hypothesis of principal valency renders these older conceptions, however, quite untenable. There can be no increase in the valency of oxygen or nitrogen when the element is simultaneously accepting an electron and giving one away. The co-ordination hypothesis of oxonium salts, which is quite in accord with modern conceptions of the structure of the atom, requires of oxygen a principal valency not greater than two and a co-ordination number not greater than three. This view runs parallel with the co-ordination hypothesis of ammonium salts where nitrogen

is regarded as remaining tervalent, but with a co-ordination number four.

The results obtained in the study of normal and hydrogen salts of the new complex alkali ion, salicylatotetramminocobalt, afford additional experimental evidence for the general hypothesis first put forward by Werner that oxonium salts and hydrated salts are analogously constituted substances and arise from a similar tendency on the part of bivalent oxygen compounds to become associated by virtue of supplementary valency with compounds containing electropositive hydrogen or metallic radicles ("Neuere Anschauungen auf dem Gebiete der Anorg. Chemie," ed. 1920, p. 264).

The new salicylatotetramminocobaltic complex contains two co-ordinating centres, the electropositive cobalt atom and the electronegative oxygen of the carbonyl group. This oxygen becomes associated either with the hydrogen of a water molecule in the hydrated normal salts (formulae I and II) or with the hydrogen of an acidic radicle in the anhydrous hydrogen salts. Of these anhydrous salts we have two classes: (1) those derived from monobasic acids—for example, the acidic dinitrate and diperchlorate (formulae XI and XII), and (2) those derived from dibasic acids, for example, the hydrogen carbonate (VIII), the hydrogen silicofluoride (X), and the biselenite (p. 1968). The only apparent exception to these generalisations is the bisulphite, which, although a hydrogen salt, is hydrated like the normal salts. This anomaly disappears, however, when it is borne in mind that sulphurous acid is a tautomeric substance



reacting in one or other of the forms symbolised in the foregoing formulae. The bisulphite of the complex salicylatocobaltamine is a derivative of the monobasic form of the acid in which the remaining hydrogen, being implicated in an electronegative complex, is not attracted by the similarly charged oxygen atom of the oxonium group. Hence the latter atom becomes co-ordinated with water as in the normal hydrated salts. It is of interest to note that the biselenite, on the contrary, is anhydrous, thus falling into line with the other anhydrous hydrogen salts.

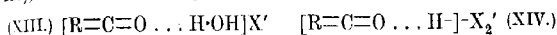
#### *Summary.*

1. The salts of the salicylatotetramminocobaltic series are well defined, soluble compounds resembling the salts of the alkali metals, so that the new salicylatocobaltamine radicle may be regarded as a compound univalent alkali ion. Its very soluble hydrated carbonate and more sparingly soluble anhydrous bi-

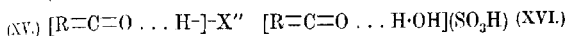
carbonate, which are both stable in the solid state, resemble the corresponding salts of sodium.

2. The salicylatotetramminocobaltic radicle is accompanied by one molecule of firmly held water of constitution in all its normal salts, of which fourteen have been examined, but it becomes anhydrous when present in its acid or hydrogen salts (5 examples) with the exception of the bisulphite, which is hydrated like the normal salts.

3. The singular variation in the state of hydration of the new salicylatocobaltamine radicle is attributed to the presence in the complex of a subsidiary co-ordinating centre due to the oxygen of the unsaturated carbonyl group. This electronegative oxygen atom co-ordinates either with water in the hydrated normal salts (XIII) or with a hydron in the acid or hydrogen salts (VIII and XI), in the latter case giving rise to anhydrous oxonium salts.



4. The present investigation has revealed the existence of two types of these oxonium salts, one series derived from monobasic acids (XIV) and the other from dibasic acids (XV).



5. The bisulphite (XVI) is exceptional in containing the hydrated form of the salicylatocobaltamine radicle (VII), probably because the hydrogen of the bisulphite group is tied up in an electronegative complex and therefore is not available for the formation of oxonium salts.

6. Hydrated salts, oxonium salts, and complex aquo-salts (for example, rosco-cobaltic and -chromic salts) are regarded as oxonium compounds containing bivalent electronegative oxygen associated co-ordinatively with compounds containing electropositive hydriions or metallic ions.

## EXPERIMENTAL.

### 1. Hydrated Normal Salts of the Salicylatocobaltamine Series.

*Salicylatotetramminocobaltic Chloride* (Formula I).—To 476 grams of hexahydrated cobalt chloride in 1 litre of water and 795 c.c. of 18N-ammonia were added successively 340 c.c. of 6N-hydrogen peroxide and 276 grams of finely powdered salicylic acid. The dark brown solution became deep red on warming at about 60° and, as the liquid cooled, reddish-violet, prismatic needles separated until a thick paste was formed. The product, after washing successively with water, alcohol, and ether, was crystallised from hot water, when the sage-green cobaltamine salicylate lake was

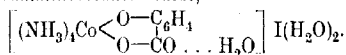


left as an insoluble impurity (12 per cent.); the filtrate yielded reddish-purple, six-sided, prismatic plates and flattened needles, which under the microscope appeared as well-defined, deep red, transparent plates and lamellæ (yield 60 per cent.). A complete analysis gave the following data: Co = 18.4;  $\text{NH}_3$  = 21.7; Cl = 11.4; C = 26.5; H = 5.8; ionic Cl = 11.5.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}_4\text{NH}_3\text{Cl}_2\text{H}_2\text{O}$  requires Co = 18.6;  $\text{NH}_3$  = 21.5; Cl = 11.2; C = 26.5; H = 5.7; ionic Cl = 11.2 per cent.

*Salicylatotetramminocobaltic chloride* was readily soluble in water to a deep red solution, evolved ammonia with hot alkalis, gave silver chloride quantitatively with silver nitrate, dissolved in cold concentrated sulphuric acid to a red solution evolving hydrogen chloride, and developed an intense green coloration with cold concentrated or warm 5*N*-nitric acid, but not with other mineral acids. This hydrated salt retained its weight even after heating for five hours at 100°. The same yield of product was obtained even with thrice the above proportion of salicylic acid, but the proportion was much diminished, with the formation of an insoluble greenish-black powder, if the liquid was boiled or if ammonium salicylate was employed in excess of aqueous ammonia.

*Salicylatotetramminocobaltic Bromide* (Formula I).—Cobaltous bromide dihydrate (327 grams) was dissolved in 300 c.c. of water and added slowly to 726 c.c. of 18*N*-ammonia. A pink crystalline precipitate appeared; the mixture was cooled in ice and 218 c.c. of 6*N*-hydrogen peroxide were added slowly with stirring. The liquid assumed a reddish-brown tint, but the pink precipitate did not dissolve until the mixture was diluted with 100 c.c. of 5*N*-ammonia and 60 c.c. of 6*N*-hydrogen peroxide. Finely powdered salicylic acid (177 grams) was then added; the dark brown solution was warmed at 50°, when it became deep red, and after further heating at 80° for fifteen minutes it was filtered while hot from a small amount of the sage green salicylic lake. The filtrate, when cooled to 0°, yielded 262 grams of purplish-red, flattened needles or plates (yield = 56 per cent.). When recrystallised from hot water, dark purple, elongated, six-sided plates were obtained which by transmitted light appeared to be transparent and deep red [Found: Co = 16.4;  $\text{NH}_3$  = 19.0; Br = 22.1; C = 23.6; H = 5.0.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\text{Br}_2\text{H}_2\text{O}$  requires Co = 16.3;  $\text{NH}_3$  = 18.8; Br = 22.1; C = 23.3; H = 5.0 per cent.]. This bromide resembled the chloride, but was rather more soluble in water.

*Salicylatotetramminocobaltic Iodide*,



—The normal iodide was best obtained by adding 5.5 c.c. of 50 per

cent. hydriodic acid and 5 c.c. of water to 6.5 grams of the bicarbonate (p. 1967). The free iodine present in the acid was removed by ether and the solution allowed to concentrate at 0° until dark, brownish-red crystals separated. The product after recrystallisation from warm water separated in dark red plates with a neutral reaction to moist litmus [Found: Co = 13.8; NH<sub>3</sub> = 15.3; I = 28.3, 28.7; H<sub>2</sub>O = 9.4. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>I(H<sub>2</sub>O)<sub>3</sub> requires Co = 13.3; NH<sub>3</sub> = 15.3; I = 28.6; 2H<sub>2</sub>O = 8.1 per cent.]. An attempt to prepare this compound by the method employed in the case of the chloride and bromide led to a product which contained excess of hydrogen iodide and appeared to consist mainly of an acidic iodide.

Cobaltous iodide dihydrate (34.9 grams) was dissolved in 35 c.c. of water, and 57 c.c. of 18N-ammonia were added, when a heavy, dark brown precipitate separated. To the mixture cooled in a freezing mixture were added very slowly 17 c.c. of 6N-hydrogen peroxide. Iodine was liberated, with consequent formation of nitrogen iodide. A further 25 c.c. of 18N-ammonia were added to remove this explosive compound, and then successively a further 10 c.c. of 6N-hydrogen peroxide and 13.8 grams of powdered salicylic acid. On heating at 75° for fifteen minutes, the dark muddy liquid cleared and became deep red. Nothing separated on cooling the filtered solution at 0° until the liquid had been concentrated considerably over calcium chloride, when irregular, dark red crystals appeared in a green scum of the sage-green lake mixed with tri-iodophenol. This insoluble residue, after washing with warm benzene and ether, was dissolved in hot water, when the acidic cobaltamine iodide crystallised in brownish-red, irregular plates (yield 14 per cent.) [Found: Co = 13.3; NH<sub>3</sub> = 15.2; I = 41.1. {C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>I<sub>2</sub>HI requires Co = 13.0; NH<sub>3</sub> = 15.0; I = 41.9 per cent.]. This preparation was strongly acidic to moist litmus.

The normal *salicylatotetramminocobaltic iodide* resembled the chloride and bromide in many physical and chemical properties; but it was much more soluble in water, contained additional water of crystallisation, and tended to form uncrystallisable syrups.

*Salicylatotetramminocobaltic Mercurihaloids*.—1. *Mercurichloride*,  

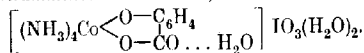
$$\left[ \begin{array}{c} (\text{NH}_3)_4\text{Co} < \text{O}-\text{C}_6\text{H}_4 \\ \text{O}-\text{CO} \dots \text{H}_2\text{O} \end{array} \right]_2 [\text{Hg}_2\text{Cl}_8].$$
 Mercuric chloride (5.4 grams), dissolved in 50 c.c. of 50 per cent. alcohol, was added to 6.3 grams of the foregoing chloride in 40 c.c. of hot water. On cooling the solution, glistening purple plates separated, weighing 6 grams. When recrystallised from hot water, the *mercurichloride*, which separated in well-defined, dark purple plates, was much

less soluble than the simple chloride (Found: Co = 8.1;  $\text{NH}_3$  = 9.3; Hg = 42.4; Cl = 19.8.  $[\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4]_2[\text{Hg}_3\text{Cl}_3](\text{H}_2\text{O})_2$  requires Co = 8.1;  $\text{NH}_3$  = 9.4; Hg = 41.6; Cl = 19.6 per cent.).

2. *Mercuribromide*,  $\left[ (\text{NH}_3)_4\text{Co} \begin{array}{c} \text{O}-\text{C}_6\text{H}_4 \\ \text{O}-\text{CO} \dots \text{H}_2\text{O} \end{array} \right]_2 [\text{Hg}_3\text{Br}_3]$ . Mercuric bromide, dissolved in warm alcohol, was added to a hot aqueous solution containing the same weight of the foregoing bromide. On cooling, the *mercuribromide* separated in dark purple scales; it was recrystallised from hot water and obtained in glistening, dark purple plates, much less soluble than the simple bromide (Found: Co = 6.7;  $\text{NH}_3$  = 7.5; Hg = 33.3; Br = 35.7.  $[\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4]_2[\text{Hg}_3\text{Br}_3](\text{H}_2\text{O})_2$  requires Co = 6.5;  $\text{NH}_3$  = 7.5; Hg = 33.4; Br = 35.5 per cent.).

3. *Mercuri-iodide*,  $\left[ (\text{NH}_3)_4\text{Co} \begin{array}{c} \text{O}-\text{C}_6\text{H}_4 \\ \text{O}-\text{CO} \dots \text{H}_2\text{O} \end{array} \right]_2 [\text{HgI}_4]$ . Salicylatotetramminocobaltic bicarbonate (p. 1967) (6.5 grams) was dissolved in 5.5 c.c. of 50 per cent. hydriodic acid and 5 c.c. of water, the free iodine being removed by ether. The blood-red aqueous layer, from which the iodide did not separate after three hours on ice, was divided into two equal parts, one of which was ground up with 4.6 grams of freshly precipitated mercuric iodide. Much of this mercury salt remained undissolved until the second part of the complex iodide solution was added, when the mercuric compound disappeared rapidly and was replaced by a heavy, purple, crystalline powder, which crystallised from a large volume of hot water in sparingly soluble, glistening, purplish-black, wedge-like, elongated prisms (Found: Co = 9.4;  $\text{NH}_3$  = 10.8; Hg = 15.0; I = 40.1.  $[\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4]_2[\text{HgI}_4](\text{H}_2\text{O})_2$  requires Co = 9.3;  $\text{NH}_3$  = 10.7; Hg = 15.8; I = 40.0 per cent.). These three well-crystallised mercurihaloids were deep red by transmitted light, their solubility decreased from chloride to iodide, they developed the characteristic intense green coloration with concentrated nitric acid, but the colour produced with the iodide changed rapidly to yellow owing to liberation of iodine.

*Salicylatotetramminocobaltic Iodate*,



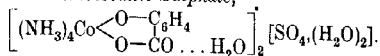
—This salt was prepared in 82 per cent. yield by adding 3.52 grams of iodic acid (1 mol.) in 20 c.c. of water to a suspension of 6.5 grams of the bicarbonate in 10 c.c. of water. Carbon dioxide was evolved and the deep red liquid set to a hard red mass, to which 20 c.c. of water were added and the mixture ground up to a thin paste. The insoluble product, consisting of purplish-red plates, pale purplish-pink by transmitted light, was moderately soluble in water to a red solution, from which silver nitrate precipitated

white silver iodate [Found: Co = 12.1;  $\text{NH}_3$  = 13.8; I = 25.9,  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\text{IO}_3(\text{H}_2\text{O})_3$  requires Co = 12.0;  $\text{NH}_3$  = 13.8; I = 25.8 per cent.].

*Salicylatotetramminocobaltic iodate* resembles the normal alkali iodates in its tendency to combine with more iodic acid to form an acid iodate.

*Salicylatotetramminocobaltic Nitrate* (Formula II).—Salicylic acid (27.6 grams) was added to 190 c.c. of cobaltamine nitrate reagent ( $\equiv$  11.8 grams Co) and the brown mixture warmed at  $70^\circ$  for ten minutes until it became deep red and deposited successively two crops of the sage green salicylate lake (7 per cent. yield). The filtrate, concentrated over calcium chloride under reduced pressure and slightly acidified with 2N-nitric acid, yielded 18 grams of roseocobaltic nitrate (30 per cent. yield). The final mother-liquor, evaporated to complete dryness at the ordinary temperature, furnished 51 grams of brown powder, which was redissolved in the minimum amount of water. The salicylatotetrammine nitrate was precipitated by alcohol as a very hygroscopic, brownish-buff precipitate and dried over calcium chloride [Found: Co = 15.8;  $\text{NH}_3$  = 17.9;  $\text{H}_2\text{O}$  at  $100^\circ$  = 9.0.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\text{NO}_3 \cdot 3\text{H}_2\text{O}$  requires Co = 15.6;  $\text{NH}_3$  = 17.9;  $2\text{H}_2\text{O}$  = 9.5 per cent.]. The third molecular proportion of water was retained up to  $135^\circ$ .

*Salicylatotetramminocobaltic Sulphate*,



—The sulphate of the new series proved to be extremely soluble and attempts at preparing it from salicylic acid and cobaltamine reagent gave only a 13 per cent. yield of the required salt, the other products being roseocobaltic sulphate (48 per cent.) and the sage green lake (5 per cent.), but by decomposing salicylatotetramminocobaltic bicarbonate with the calculated amount of 10 per cent. sulphuric acid this sulphate was readily obtained in small, bright damask-red plates, the yield being 92 per cent. (Found: Co = 16.9;  $\text{NH}_3$  = 19.5; S = 5.2;  $\text{H}_2\text{O}$  at  $100^\circ$  = 5.8.  $[\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4]_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  requires Co = 17.0;  $\text{NH}_3$  = 19.6; S = 4.6;  $2\text{H}_2\text{O}$  = 5.2 per cent.). The remaining water was retained up to  $135^\circ$ .

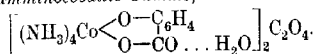
*Salicylatotetramminocobaltic sulphate* was extremely soluble in water to a deep red solution very prone to become supersaturated, so that, owing to slow decomposition, the salt could not be recovered, as it yielded the sage green lake. With concentrated nitric acid the sulphate solution developed the characteristic green coloration exhibited by all the preceding and following salts of the salicylato-series.

*Salicylatotetramminocobaltic Silicofluoride* (Formula IX).—A slight

deficiency of 5*N*-hydrofluosilicic acid was added to a 30 per cent. solution of the bicarbonate followed by a few drops of alcohol, when the liquid set to a thick crystalline paste consisting of purplish-rose, micaceous plates of the normal silicofluoride, which were very soluble in water but insoluble in alcohol or ether [Found: Co = 15.7; NH<sub>3</sub> = 18.4; F = 15.1. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>SiF<sub>6</sub>·4H<sub>2</sub>O requires Co = 15.9; NH<sub>3</sub> = 18.4; F = 15.4 per cent.].

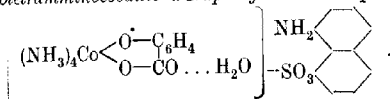
In this salt and in the hydrogen silicofluoride the fluorine was estimated volumetrically by adding excess of calcium chloride to solutions of the silicofluorides, when calcium fluoride was produced and the equivalent amount of hydrochloric acid was set free; the latter was titrated with standard alkali.

*Salicylatotetramminocobaltic Oxalate*,



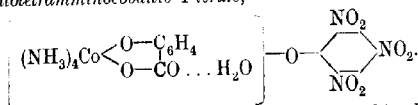
—This salt was obtained in 80 per cent. yield by adding the calculated amount of oxalic acid to a 60 per cent. solution of the normal carbonate; it consisted of dark red, flattened needles or plates, only moderately soluble in water [Found: Co = 18.4; NH<sub>3</sub> = 20.9; C<sub>2</sub>O<sub>4</sub> = 13.2. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O requires Co = 18.2; NH<sub>3</sub> = 20.9; C<sub>2</sub>O<sub>4</sub> = 13.5 per cent.].

*Salicylatotetramminocobaltic α-Naphthylamine-8-sulphonate*,



—The α-naphthylamine-8-sulphonate was obtained as a heavy, crystalline, dark red powder on adding 2.2 grams of Schölkopf acid to 3.24 grams of the bicarbonate dissolved in 15 c.c. of warm water, the reagents being thoroughly mixed in a mortar. This salt, which was practically insoluble in water, consisted of small, dark red plates (Found: Co = 11.6; NH<sub>3</sub> = 13.8. [C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>][C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>NS]·H<sub>2</sub>O requires Co = 11.7; NH<sub>3</sub> = 13.5 per cent.).

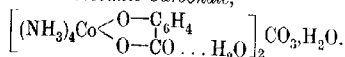
*Salicylatotetramminocobaltic Picrate*,



—A solution of 8.5 grams of the cobaltamine bicarbonate in 18 c.c. of water was stirred with considerable excess of picric acid, the mixture evolved carbon dioxide, but only on warming, and a heavy precipitate consisting of dark brownish-red plates was deposited; this was freed from picric acid and ammonium picrate by prolonged extraction with cold water and acetone and subse-

quent washing with alcohol and ether. The product, when crystallised from hot water, separated in glistening, brownish-red, six-sided prisms or plates, bright red by transmitted light [Found : Co = 11.7;  $\text{NH}_3$  = 13.4.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\cdot\text{C}_6\text{H}_2\text{O}_7\cdot\text{N}_3\cdot\text{H}_2\text{O}$  requires Co = 11.6;  $\text{NH}_3$  = 13.4 per cent.].

*Salicylatotetramminocobaltic Carbonate,*



—A solution of the carbonate (6.5 grams) in 10 c.c. of water, prepared by treating the bromide with moist silver carbonate, was diluted with an equal volume of alcohol, the solution cooled to  $0^\circ$ , and treated slowly with 5 c.c. of ether. A pink, amorphous precipitate appeared which rapidly became dark red and crystalline. After two days in the ice-chest, this precipitate was collected (3.8 grams or 58 per cent. of theory). It consisted of purplish-red, micaceous plates, pale red by transmitted light, and was very soluble in water. The solution was strongly alkaline to litmus and methyl-orange; it gave an immediate precipitate with barium chloride and evolved carbon dioxide on acidifying [Found : Co = 18.4;  $\text{NH}_3$  = 21.2;  $\text{CO}_2$  = 6.8.  $\text{C}_{14}\text{H}_6\text{O}_6\text{Co}_2(\text{NH}_3)_8\text{CO}_3(\text{H}_2\text{O})_3$  requires C = 18.4;  $\text{NH}_3$  = 21.2;  $\text{CO}_2$  = 6.9 per cent.].

## II. Anhydrous Hydrogen Salts of the Salicylatocobaltamine Series.

*Salicylatotetramminocobaltic Bicarbonate* (Formula VIII).—This salt, the key to the preparation of many other normal and acid salts of the series, was prepared by triturating 63.3 grams of salicylatotetramminocobaltic chloride for one hour with freshly prepared silver carbonate and 35 c.c. of water. The mixture changed from dark red to pink, and a slight odour of ammonia was noticed. The filtrate from silver chloride was a deep red, highly alkaline solution containing the very soluble normal carbonate. On saturating with carbon dioxide, the liquid set to a stiff purplish-red paste of small, glistening plates (45 grams or 75 per cent.). This bicarbonate was recrystallised from dilute alcohol saturated with carbon dioxide [Found : Co = 18.3;  $\text{NH}_3$  = 21.1;  $\text{CO}_2$  = 13.2.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\text{CO}_3\text{H}$  requires Co = 18.2;  $\text{NH}_3$  = 21.0;  $\text{CO}_2$  = 13.6 per cent.].

The bicarbonate obtained in dark red plates was slightly alkaline to litmus and was moderately soluble in water, evolving carbon dioxide on warming. It gave no precipitate with calcium chloride in the cold, but calcium carbonate was deposited on boiling.

Attempts to prepare salicylatotetramminocobaltic hydroxide with the chloride and moist silver oxide led to decomposition of the co-ordination complex and liberation of ammonia.

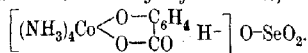
*Salicylatotetramminocobaltic Hydrogen Silicofluoride* (Formula X).—This hydrogen salt was prepared by adding excess of 5*N*-hydrofluosilicic acid to a 30 per cent. solution of the bicarbonate, when after one hour a mass of red crystals was obtained having a bright brownish-red tint by transmitted light (Found: Co = 14.4; NH<sub>3</sub> = 16.8; F = 28.2. [C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>]SiF<sub>6</sub>H requires Co = 14.5; NH<sub>3</sub> = 16.8; F = 28.1 per cent.).

*Salicylatotetramminocobaltic Hydrogen Dinitrate* (Formula XI).—This acid nitrate was prepared in 68 per cent. yield by dissolving the bicarbonate in the equivalent amount of 2.5*N*-nitric acid and by adding a further equivalent amount of 4*N*-nitric acid. The solution then set to a purple-red, crystalline paste consisting of bright rose-red aggregates of glistening plates, which were stable in air, thus differing from the hygroscopic normal nitrate [Found: Co = 15.0; NH<sub>3</sub> = 17.3; HNO<sub>3</sub> = 15.8. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>H(NO<sub>3</sub>)<sub>2</sub> requires Co = 15.2; NH<sub>3</sub> = 17.5; HNO<sub>3</sub> = 16.2 per cent.].

*Salicylatotetramminocobaltic Hydrogen Diperchlorate* (Formula XII).—Two equivalents of 2*N*-perchloric acid were added to the bicarbonate, a blood-red solution was formed which speedily set to a crystalline paste consisting of reddish-brown, glistening plates stable in air and moderately soluble in water to a deep red, intensely acid solution [Found: Co = 12.7; NH<sub>3</sub> = 14.7; HClO<sub>4</sub> = 21.9. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>H requires Co = 12.7; NH<sub>3</sub> = 14.7; HClO<sub>4</sub> = 21.7 per cent.].

The normal perchlorate could not be isolated owing in all probability to its extreme solubility in water or alcohol.

*Salicylatotetramminocobaltic Hydrogen Selenite*,



—The bicarbonate (6.5 grams) was ground up with 2.6 grams of selenious acid (1 mol.) and 10 c.c. of water. Carbon dioxide was evolved and a deep red solution was formed, from which nothing separated even on addition of alcohol. A further 2.6 grams of selenious acid in 5 c.c. of water was added together with an equal bulk of alcohol. From the solution, cooled in the ice-chest, dark red needles separated slowly. These crystals were readily soluble in water to a dark red solution which yielded red selenium on adding sulphurous and hydrochloric acids [Found: Co = 15.2; NH<sub>3</sub> = 17.2; Se = 20.3. C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>Co(NH<sub>3</sub>)<sub>4</sub>SeO<sub>3</sub> requires Co = 15.1; NH<sub>3</sub> = 17.4; Se = 20.2 per cent.].

### III. *Salicylatotetramminocobaltic Hydrogen Sulphite* (Formula VII).

The bisulphite was produced in 92 per cent. yield by passing excess of sulphur dioxide into a suspension of the bicarbonate

(9.7 grams) in 15 c.c. of water. An equal volume of alcohol was added and the solution cooled in ice, when red needles separated. Recrystallised from hot dilute alcohol saturated with sulphur dioxide, the salt separated in dark purplish-red, acicular prisms, moderately soluble in water and distinctly acid to litmus; it evolved sulphur dioxide with dilute acids [Found: Co = 16.3;  $\text{NH}_3$  = 18.6; S = 8.9.  $\text{C}_7\text{H}_4\text{O}_3\text{Co}(\text{NH}_3)_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$  requires Co = 16.3;  $\text{NH}_3$  = 18.8; S = 8.9 per cent.].

#### IV. The Colour Reaction of the Salicylatotetramminocobaltic Salts.

The red salicylatocobaltamine salts described in the present paper, when treated with 8*N*-nitric acid (5 mols.), dissolved to a dark green solution, the colour of which was so intense that it was still perceptible at a dilution of 1 part of cobalt in six million parts of water. This coloration, which is one of the most delicate colour reactions of cobalt, has served as a useful test in the preparation of the salicylatocobaltamines. By using the bicarbonate and working in strong solutions, the dark emerald-green product has been isolated in solid granular form. The nature of the chemical change has not been completely elucidated; it is, however, certainly complex, leading to alteration of the cobaltamine complex and nitration of the salicylate group, 5-nitrosalicylic acid having been identified among the decomposition products of the green substance. This colour reaction is still under investigation.

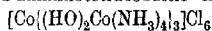
#### V. The Cobaltamine Reagent.

The reagent employed in our earlier researches on cobaltamine lakes (*loc. cit.*) and in the production of salicylatotetramminocobaltic chloride was prepared and identified as follows: An ice-cold solution of 23.8 grams of cobalt chloride,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (Co = 5.9 grams), and 8.5 c.c. of 12*N*-hydrogen peroxide ( $\text{H}_2\text{O}_2$  = 1.7 grams) in 15 c.c. of water was added slowly to 57 c.c. of 18*N*-ammonia ( $\text{NH}_3$  = 15.3 grams) maintained at 0°. On evaporating nearly to dryness over calcium chloride, the intensely dark brown solution yielded 19 grams (76 per cent.) of flattened, reddish-purple needles. This product, which was found to be hydroxopentamminocobaltic chloride,  $[\text{HO}\cdot\text{Co}(\text{NH}_3)_5]\text{Cl}_2\cdot\text{H}_2\text{O}$  (Werner, *Ber.*, 1907, 40, 4098), was characterised by adding solid potassium iodide to its concentrated aqueous solution, when the brownish-purple hydroxopentamminocobaltic iodide separated (Found: Co = 14.1.  $[\text{HO}\cdot\text{Co}(\text{NH}_3)_5]\text{I}_2$  requires Co = 14.2 per cent.).

When in the foregoing preparations the reagents were not cooled, only 65 per cent. of the monohydroxo-derivative was obtained



together with 8 per cent. of a mixture of purpureo- and roseo-cobaltic chlorides. The other products were uncrystallisable and remained on concentration in the dark red strongly alkaline syrup, which probably contained highly basic salts including Werner's hexahydroxododeca-amminotetracobaltic chloride,



(Ber., 1907, 40, 2103).

VI. *Note on the Preparation of Hexamminocobaltic Chloride (Luteo-cobaltic Chloride) in the Rotating Autoclave.*

The various cobaltamines can be converted readily into hexamminocobaltic chloride, the final stage of ammination, by digestion with aqueous ammonia in the rotating autoclave (T., 1920, 117, 780).

1. *From Chloropentamminocobaltic Chloride (Purpureocobaltic Chloride).*—A 400 c.c. open bottle containing 25 grams of purpureo-chloride, suspended in 100 c.c. of 18*N*-ammonia, was tightly packed by means of asbestos cord into the rotating autoclave. The temperature was raised gradually to 100° (pressure 30 lb. per sq. in.) and then to 120° (45 lb. pressure). After thirty minutes at the higher temperature, the autoclave was stopped and cooled. The bottle then contained a mass of large, reddish-brown crystals of hexamminocobaltic chloride. The mother-liquor, on addition of an equal bulk of alcohol, yielded a further crop of this salt (total yield = 25 grams or 90 per cent.).

2. *From the Cobaltamine Reagent.*—By this method one can proceed directly from a cobaltous salt. An open 500 c.c. bottle, packed securely in the autoclave, was charged in succession with 24 grams of hexahydrated cobalt chloride dissolved in 100 c.c. of water, 85 c.c. of 15*N*-ammonia, 16 grams of ammonium chloride in 50 c.c. of water, and 20 c.c. of 5*N*-hydrogen peroxide. The dark brown solution was heated slowly during one and a half hours to 140° (100 lb. pressure) and the autoclave then cooled. A crop of the orange luteo-chloride was separated, and the mother-liquor acidified slightly with 10*N*-hydrochloric acid, when a further crop was obtained (total 20 grams). The filtrate was then used to dissolve 24 grams of hexahydrated cobalt chloride, and 85 c.c. of 15*N*-ammonia and 20 c.c. of 5*N*-hydrogen peroxide were added. The brown solution was heated during one and a half hours to 164° (150 lb. pressure). After cooling, 29 grams of large, brownish-orange crystals of luteo-chloride were collected and dried at 100° (total yield from the two successive heatings = 49 grams or 91 per cent.).

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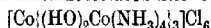
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# CCXXXVI.—*Thermal Expansion of Gelatin Gels.*

By ALAN TAFTEL.

IN their determinations of the expansion of various glasses on heating, Peters and Cragoe (*Scientific Papers, Bur. of Standards*, No. 393), on plotting expansion against temperature, obtained curves which were roughly linear for a considerable range of temperature, and then, within a region which never exceeded 40°, changed direction, still continuing linear and indicating a two- to seven-fold increase in the expansion. About 75° above this "critical region" the glass softened and contracted.

The object of the present research was to discover whether gels, gelatin gels in particular, showed the same behaviour when heated to their melting point.

A preliminary experiment was tried with an instrument of the shape of the ordinary glass bulb-thermometer. The gelatin sol was introduced into the bulb, allowed to set, and covered with mercury, and the whole was then warmed in a well-stirred bath of water at the rate of 2° per hour until the temperature reached 30°. When the readings in the capillary stem were plotted against temperature, a curve was obtained which appeared to consist of two linear portions joined by a fairly sharp bend at about 21°; the difference of slope between the two was, however, not very great; the change of slope was in the direction of increased expansion. This gel was of 10 per cent. concentration of gelatin by weight. A second measurement with a 15 per cent. gel gave a smooth curve with no indication of a break.

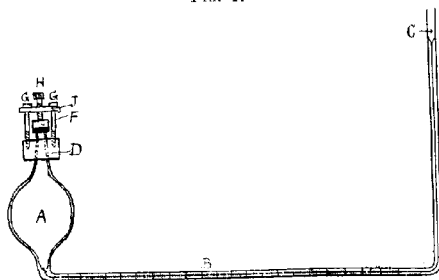
A more accurate instrument was now designed; the form which it assumed finally is that shown in Fig. 1.

It consists of a glass bulb, *A*, of 85 c.c. capacity, to which is attached a graduated capillary tube, *B*, of area of cross section a little more than 0.02 sq. cm. The capillary is bent upwards and terminates in a glass tube, *C*. The bulb of the dilatometer is closed by a brass disk, *F*, to the underside of which is cemented a small

circle of rubber sheeting. This cap is pressed down on the opening of the bulb by the arrangement of screws shown; *D* is a collar of copper cemented with fusible metal to the neck of the dilatometer; the two screws, *G G*, turn about halfway in the collar; the brass disk, *J*, can slide up and down along these screws, whilst *H* screws into *J*. Thus by tightening up *G G* and then *H*, the cap is pressed firmly down, and the bulb closed securely, without danger of letting in air or water. A stopcock had been tried in place of this arrangement, but was found to be unsatisfactory owing to the action of warm water on the lubricant.

The capillary tube, *B*, was calibrated, previously to sealing to the bulb, by joining to it a capillary tap, and surrounding the upper part of the burette thus made by a jacket of circulating water at constant temperature. The tube was filled with clean

FIG. 1.



dry mercury, and portions of this were run out and weighed, readings of the different levels of the meniscus being made with a cathetometer fitted with a micrometer eyepiece. Each centimetre division was found to correspond, on the average, to about 0.0205 c.c.

To fill the dilatometer, a weighed quantity (about 10 c.c.) of mercury was introduced, followed by the gelatin solution, which was allowed to flow out from the jet of an inverted wash-bottle containing the gelatin into the bulb of the dilatometer via the neck, the flow being hastened when necessary by pumping air into the space above the solution. The introduction of air-bubbles and froth was avoided by allowing the inverted bottle to stand, the rising of the bubbles to the surface of the solution being facilitated by evacuating the space above the solution. The screw cap was then closed tightly in such a way that the bulb was completely full of gelatin and mercury, and the meniscus of the latter at a convenient point of the capillary. The dilatometer was weighed to find the mass of the gel, and was then fixed in a

well-stirred thermostat with a glass front, through which the mercury meniscus, suitably illuminated, could be read with a horizontally mounted cathetometer fitted with a micrometer eyepiece. When warming, temperature lag was found to be avoided by heating in steps instead of continuously.

The thermometer used was graduated in tenths of a degree, hundredths being easily estimated, and was read through a cathetometer which could move vertically. It was standardised with ice and with sodium sulphate decahydrate, and calibrated by tapping off threads of mercury of different lengths, and running these along the bore under a travelling-microscope. The thermometer was placed vertically in the bath, with its bulb touching that of the dilatometer, and was tapped, as was likewise the capillary tube, before being read.

The gelatin used in the following experiments, unless otherwise stated, was Nelson's Photographic No. 1; it was very kindly supplied gratis by Messrs. Nelson Dale & Co. The gel was in every case prepared by soaking the air-dried gelatin in distilled air-free water for two and a half hours, which was a long enough period for the dissolution of this easily soluble brand, and dispersing on the water-bath at 50° for twenty minutes, with stirring. It was then at once brought into the dilatometer, and kept for eighteen to twenty-four hours before measurements were made.

The concentration of the gels was determined by keeping them over phosphoric oxide in a vacuum over-night, and then heating at 100° in the electric oven, in a dry atmosphere, until the weight was constant. Heating in the steam-oven did not drive off the water so readily and completely as the above method. Prolonged heating of the gelatin at 100° seems to bring about a slow decomposition, with a resulting decrease in weight.

*Calibration.*—The dilatometer was calibrated for different temperatures by bringing into it about 10 c.c. of clean, dry mercury, and filling up with distilled, air-free water. The temperature of the bath was raised in steps, and time allowed for equilibrium to be attained at each step. The reverse process, that is, discontinuous cooling, was also carried out; the readings were the same as for heating. From a knowledge of the specific volumes of water and of mercury at the various temperatures, the volumes of the bulb up to the zero were calculated, with the following results:

Temp. . . . .	11·90°	15·68°	16·81°	19·41°	20·98°	22·15°
Vol. of bulb in c.c. .	84·9012	84·9102	84·9128	84·9190	84·9227	84·9246
Temp. . . . .	24·15°	26·30°	28·94°	30·10°		
Vol. of bulb in c.c. .	84·9295	84·9347	84·9411	84·9434		

If these values are plotted on a graph, the points obtained will lie



on a straight line. The mean coefficient of cubical expansion of the glass composing the bulb for the range of temperature used is, from the above,  $\frac{0.0422}{18.20 \times 84.9012} = 0.0000273$ , or the mean coefficient of linear expansion = 0.0000091.

*Measurements.*—Unless otherwise stated, the concentration of a gel is taken as the weight of dry gelatin per 100 grams of gel. A 10 per cent. gelatin was first tried, and this gave a smooth curve when its expansion was plotted against temperature. A gel of the same concentration prepared from the brand of gelatin employed in the preliminary experiments (Nelson's Commercial Leaf) was then introduced into the dilatometer, and the bath heated at the rate of 2° per hour. A smooth curve was again obtained. The experiment was repeated, and the same result obtained. No break in the curve could be made to appear, either with this or with other samples of gelatin at various concentrations, although different rates of heating were tried and the temperature was raised in steps; also, the gels were melted and then cooled very quickly or very slowly, but the curve was always of the same shape.

The curves for the gels whose expansions are tabulated below are quite regular for temperatures up to, at, and above the melting point of the gel, that is, when the gel melts there is no sudden change in volume. The curves are flatter than those for water, and the flattening is the more pronounced the more concentrated the gel.

TABLE I.  
*Expansion of gelatin gels.*

Temp.	Concentration of gel.					
	Water.	2.02%.	5.01%.	8.90%.	16.49%.	24.81%.
	Vol. of 1 gram in c.c.	Vol. of 1 gram in c.c.	Vol. of 1 gram in c.c.	Vol. of 1 gram in c.c.	Vol. of 1 gram in c.c.	Vol. of 1 gram in c.c.
15.00°	1.000874	0.994158	0.984345	0.970959	0.946113	0.918213
17.00	1.001200	0.994497	0.984702	0.971364	0.946568	0.918783
19.00	1.001571	0.994880	0.985110	0.971815	0.947085	0.919400
21.00	1.001985	0.995294	0.985572	0.972308	0.947660	0.920035
22.00	1.002208	0.995533	0.985815	0.972601	0.947994	0.920400
24.00	1.002685	0.996030	0.986360	0.973183	0.948672	0.921135
26.00	1.003201	0.996563	0.986941	0.973792	0.949380	0.921891
28.00	1.003755	0.997129	0.987546	0.974401	0.950095	0.922660
30.00	1.004346	0.997742	0.988190	0.975057	0.950834	0.923442
32.00	1.004972	0.998359	0.988820	0.975729	0.951589	0.924245

*Mean Coefficient of Expansion.*—The mean coefficients of expansion between 15° and 32° for the different gels given below are obtained by dividing the increase in volume between the two

temperatures by the product of the volume at 15.00° and the temperature range.

Conc. of gel.	Mean coeff. of exp. (15—32°).	Conc. of gel.	Mean coeff. of exp. (15—32°).
24.81	0.0003864	5.04	0.0002674
16.49	0.0003407	2.02	0.0002486
8.90	0.0002891	0.00 (pure water)	0.0002414

The results show that the mean coefficient of expansion increases with increasing concentration of the gel, being, for a 25 per cent. gel, more than one and a half times as great as for pure water. If coefficients are plotted against concentrations, the relation between the two is seen to be a linear one.

*Specific Volume.*—When the volumes of 1 gram of gel at 15.00° and at 32.00°, respectively, are plotted against concentration, two straight lines are obtained, which diverge slightly as the concentration increases.

*Purified Gelatin.*—As much as possible of the impurities contained in the Photographic No. 1 brand of gelatin was removed by washing in running tap-water for thirty hours, and after this with very many changes of distilled water. The swelled gelatin was dispersed as usual, and its expansion measured. The values given for the unwashed gel are those interpolated from the specific volume-concentration curve.

Conc. of gel.	Temp.	Vol. of 1 gram in c.c.	
		Purified gel.	Unwashed gel.
10.35	15.00°	0.968362	0.9665
"	21.00	0.969737	"
"	26.00	0.971240	—
"	32.00	0.973251	0.9715

It is seen that the specific volumes of the purified gel are larger than those of the impure gel. The mean coefficient of expansion of the former for the range 15—32° is 0.000297, of the latter 0.000304.

#### *Effect of Hydrogen-ion Concentration on Expansion.*

A 10 per cent. gel was introduced into the dilatometer, and its expansion measured. Concentrated hydrochloric acid was added to make the concentration of acid in the bulb 0.02*N*, the cap closed down, and the whole kept over-night; the expansion was then measured, the change of volume of the contents of the bulb caused by the addition of the acid being a very slight one. More acid was introduced to make the solution 0.15*N*, and a measurement again made, and again with 0.15*N*-acid. In each case the coefficient of expansion of the gel was found to be practically unchanged by

the acid. A second series of measurements was made with well-washed gelatin, acid being added to give 0.01*N*- and 0.03*N*-solutions. As before, there was no change in expansion, although it was thought that since gelatin swells to a much greater extent in acid solutions of these concentrations than in pure water, there might have been some accompanying effect on the expansion of the gels.

#### *Expansion of Dry Gelatin.*

It has been shown that the coefficient of expansion of a gel is greater than that of pure water, and increases linearly with increasing concentration of the gel. We may now inquire whether this is due to the possession by gelatin itself of a coefficient of expansion larger than that of water.

The specific volume of solid gelatin was accurately determined at 18°, 25°, and 32° in a specific gravity bottle, toluene being used as the displaced liquid. The bottle was calibrated with air-free distilled water, and also with pure dry toluene, at these three temperatures. Air-dry gelatin, cut into small pieces, was heated at 100° in a dry atmosphere for thirty hours (sample A), and for forty hours (sample B). The toluene was dried over phosphoric oxide and distilled therefrom into a receiver protected from atmospheric moisture by a calcium chloride tube. The values obtained were:

Temp.	Vol. of 1 gram of dry gelatin in c.c.	
	Sample A.	Sample B.
18.00°	0.7417	0.7417
25.00	0.7430	0.7429
32.00	0.7445	0.7445

These values agree very closely. The mean coefficient of expansion of dry gelatin is, from the above, 0.000271; that for water for the same range is 0.000241; that is, gelatin expands somewhat more rapidly with rising temperature than does water. But when it is considered that, for instance, the coefficient of a 25 per cent. gel is 0.000386, and that only one-quarter by weight of this gel consists of gelatin, it is evident that, unless the coefficient for gelatin increases to an extremely large degree when gelatin is associated with water in a gel, it is not to the expansion of the gelatin that we must look for the cause of the large coefficients possessed by the gels.

Lüdeking (*Ann. Phys. Chem.*, 1888 [iii], **35**, 552) determined the density of gelatin gels by weighing them in air and in water, and showed that the density of the gel is greater than that calculated additively from the densities of its constituents. He ascribed this to a powerful contraction of the water in the gel.

In Table II is given the total contraction in volume (as calculated from the results given in Table I and the density of dry gelatin at different temperatures) resulting when water in requisite amount is added to 1 gram of dry gelatin to give gels of the concentrations tabulated. It will be seen that, at any one temperature, this contraction is constant. That is, 1 gram of dry gelatin always causes the same total contraction of the gel, no matter with how much water it is associated. At 15°, whether 3 c.c. of water or 50 c.c. are added, the *total* contraction is 0.073 c.c.; and at 32° the contraction is 0.065 c.c.

This implies, of course, that the relation between the contraction of a gel containing 1 gram of water and the concentration of the gel expressed as grams of gelatin per 1 gram of water is given by the simple equation: contraction =  $a \times$  concentration, where  $a$  is a constant for any one temperature, but itself decreases with rising temperature. In fact, if contraction and concentration are plotted against each other, a straight line is obtained as the curve for 15°, and another straight line for 32°, the two lines passing through the point for water (that is, zero grams of gelatin per gram of water, and zero contraction) and diverging rapidly with increasing concentration. That the curves pass through the water-point indicates that the measurements are accurate. It can also easily be shown that the contraction for any one gel decreases practically linearly with rising temperature.

TABLE II.

Temp. 15.00°.

Conc. of gel. Weight per cent.	C.c. of water added to 1 gram of gelatin.	Sum of vols. of added water and of 1 gram of gelatin.	C.c. of gel containing 1 gram of gelatin.	Contraction of gel containing 1 gram of gelatin.	Mean = 0.073
24.81	3.0335	3.7747	3.7009	0.0738	
16.49	5.0684	5.8096	5.7374	0.0722	
8.90	10.2442	10.9854	10.9101	0.0753	
5.04	18.8580	19.5992	19.5298	0.0694	
2.02	49.0479	49.7891	49.7158	0.0733	

Temp. 32.00°.

24.81	3.0456	3.7900	3.7251	0.0649	Mean = 0.065
16.49	5.0899	5.8344	5.7708	0.0636	
8.90	10.2858	11.0303	10.9629	0.0674	
5.04	18.9341	19.6786	19.6171	0.0615	
2.02	49.2461	49.9906	49.9237	0.0669	

If this contraction is an actual contraction of one or both of the constituents of the gel, then

- (1) Both gelatin and water may be contracted.

- (2) Considering the water only, the whole of the water in the gel may be uniformly contracted, the greater the quantity of water the less is the contraction per c.c.; or
- (3) A portion only of the water in the gel is contracted, this portion being in amount the same per fixed weight of gelatin for gels of different concentration; in other words, there is a layer of compressed water about the gelatin particles, and this layer is not affected in amount by varying the amount of water in the gel.

It is difficult to realise in what way the attractive force which gelatin exerts on water, and vice versa, can distribute itself uniformly throughout all the water molecules present, decreasing regularly in intensity as the water content increases. It seems, on the other hand, very probable that only a part of the total water is contracted, and that when dry gelatin has taken up this amount of water, any additional water imbibed by it is not contracted, or only very slightly. Possibly the condensed water, by its attraction for the gelatin particles, may decrease the cohesion existing between the particles in the dry solid, thus causing the separative tendency of the kinetic energy of translation of these particles to become more effective, and, in the presence of an excess of water, enabling the particles to move apart to some new position of equilibrium; that is, the gelatin swells to a definite limit, the uncontracted water being retained in the "pores" thereby developed.

There is a possibility that the contraction resulting from the bringing together of gelatin and water is not due to an actual contraction of either, but to a filling up of pores which may exist in solid gelatin. Since a contraction was observed when the specific volume of gelatin was determined under toluene, evidently toluene cannot enter these pores. If the observed contraction is a measure of the volume of the pores, then this volume will be 0.073 c.c. at 15° and 0.065 c.c. at 32° per 1 gram of gelatin. The volume of 1 gram of gelatin under toluene is 0.7412 c.c. at 15° and 0.7445 c.c. at 32°. The actual specific volume of gelatin should be, therefore,  $0.7412 - 0.073 = 0.668$  c.c. at 15°, and  $0.7445 - 0.065 = 0.680$  c.c. at 32°, which would give for the mean coefficient of expansion of dry gelatin between 15° and 32° the enormous value  $\frac{0.012}{0.668 \times 17} = 0.0106$ . It is very improbable that this is the actual coefficient for dry gelatin; and it seems, then, that the contraction cannot be attributed to a penetration of pores in solid gelatin by water.

From Table II, it will be seen that the contraction of a gel decreases with temperature the more rapidly the more concentrated

the gel, since, in the case of a 25 per cent. gel, 3.7009 c.c. at 15° suffer a decrease in contraction of 0.008 c.c. when heated to 32°, whereas, in the case of a 2 per cent. gel, the same decrease is spread over 49.7158 c.c. It is evidently due to this that the coefficient of expansion of a gelatin gel increases with its concentration and is greater than that of water. In measuring the thermal expansion of a gel, we are superposing three volume changes; the expansion of the gelatin, the expansion of the water, and the decrease of contraction of the gel.

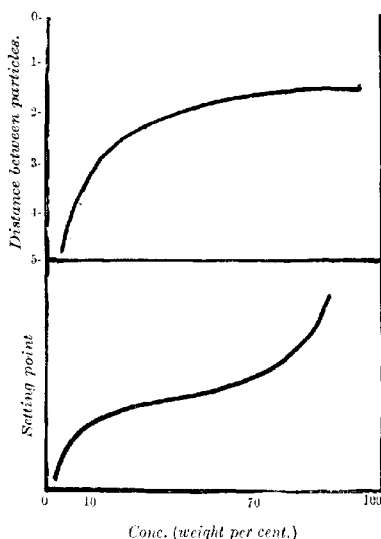
The experiments of Schroeder (*Z. physikal. Chem.*, 1903, 45, 75) on the imbibition of water and of water vapour by dry gelatin also suggest that only a fraction of the water in a gelatin gel is contracted. He found that a plate of dry gelatin, suspended in an atmosphere saturated with water-vapour, took up less than one-half its weight of water after twenty days. The plate was then immersed in water, when, after one hour, it imbibed six times its weight of water. The figures he gives for vapour absorption are, 0.904 gram of dry gelatin absorbs 0.374 gram of water, or 1.000 gram of gelatin absorbs 0.414 gram of water. If we are justified in assuming that it is this amount of water which is the portion of water in each gel contracted, then at 15° 0.414 gram of water decreases in volume by 0.073 c.c. It would require an externally applied pressure of 12,000 or more atmospheres to produce this contraction in water.

It may not be considered irrelevant, perhaps, to discuss, at this point, an interesting curve expressing the relationship between setting point and concentration of gelatin jellies (Sheppard and Sweet, *J. Ind. Eng. Chem.* 1921, 13, 413).

The curve is of the type shown in Fig. 2, and contains a double flexure, one at about 10 per cent., the other at about 70 per cent. concentration. Now a rough estimation of the distance apart of the particles of gelatin in a jelly may be made by imagining the volume of jelly containing 1 gram of gelatin to be in the shape of a cube, and that we have  $n^3$  particles distributed evenly over this volume. The distance apart of the particles will be approximately  $\sqrt[3]{\text{volume}/n}$ . If these distances are plotted against concentration (weight per cent.), a hyperbola is obtained (Fig. 2). If, then, the setting point (or the melting point) is dependent on the distance apart of the particles, being higher the smaller this distance, then from 0 per cent. to about 10 per cent. concentration the setting point should rise rapidly, since the distance between the particles decreases rapidly. Above 10 per cent. and up to 100 per cent., the distance decreases slowly and almost linearly, and the setting point should increase slowly and almost linearly up to 100 per cent. concentration. This is actually the case up to 70 per cent.

According to Schroeder, 0.904 gram of dry gelatin, when placed in an atmosphere saturated with water vapour, can absorb a maximum of 0.374 gram of water. The concentration of this "gel" would be  $\frac{0.904 \times 100}{1.278} = 70$  per cent. Thus, when the concentration of a gelatin gel reaches 70 per cent., the particles of gelatin in it approach each other within a distance which is of the order of the thickness of the sheath of condensed water surrounding them.

FIG. 2.



At this distance they enter into a region where very large forces come into play, and this corresponds with the second point of inflection of the curve.

*The Temperature of Maximum Density of Gelatin Gels.*

It is a familiar fact that the density of pure water passes through a maximum at about  $4^{\circ}$ . The presence of a salt or of other dissolved substance generally has the effect of lowering this temperature of maximum density; sodium chloride, for instance, produces a lowering which is proportional to the concentration of the salt in the same way as with the freezing point of water. An external

pressure applied to water also lowers the temperature of maximum density.

Scott (*J. Physical Chem.*, 1914, **18**, 677) found that gelatin depressed the temperature of maximum density of water, and the author was led to make some measurements with electrolyte-free gelatin in the dilatometer described in the first part of this paper.

The gelatin used was "Nelson's Powdered." It was purified by Smith's method (*J. Amer. Chem. Soc.*, 1921, **43**, 1350); the powdered gelatin is washed with a cold 10 per cent. solution of sodium chloride containing a little hydrochloric acid, to remove difficultly diffusible salts of calcium, iron, etc., and alkali; the concentration of the solution is then reduced to 1 per cent., no acid being now added, and the gelatin washed with this; the washing solution is made more and more dilute, and finally several litres of distilled water are used, until the water contains no trace of chlorine ion as evidenced by silver nitrate solution. The purified gelatin is dispersed at 50° for twenty minutes, and at once introduced into the dilatometer, and kept over-night.

In observing the temperature of maximum density (*t.m.d.*), the bath was brought to 0° with ice, and if a lower temperature than 0° was required, a mixture of crushed ice and salt was added to the ice-cold water. The temperature of the bath was allowed to rise slowly, and was noted when the capillary ceased receding and again when it commenced advancing, the meniscus usually remaining stationary for about 0.5°; the mean of the two temperatures was taken as the apparent temperature of maximum density. A series of readings of meniscus and thermometer was also taken round about the region of maximum density. Allowance was made for the change of volume of the glass bulb and the mercury, and by plotting the volumes of the gel at various temperatures near the temperature of maximum density against these temperatures a close estimate could be made of the real temperature of maximum density of the gel. The results obtained were as follow:

Conc. of gel. Grams of dry gelatin per 100 grams of water.	<i>T.m.d.</i>	<i>T.m.d.</i>
	by expt.	calculated.
0.00	+ 4.0°	+ 4.0°
3.60	+ 2.5	+ 2.5
7.05	+ 1.3	+ 1.5
13.00	- 1.2	- 1.0

When the concentration, expressed as above, is plotted against the lowering of the temperature of maximum density below 4°,



the four points obtained lie on a straight line, that is, for the above range of concentration, we may write:

$$\text{Lowering of } t.m.d. = \text{constant} \times \text{conc. of gel.}$$

The lowering produced by gelatin is by no means small, and compares with that effected by many non-electrolytes (Landolt-Börnstein, "Physikalisch-Chemischen Tabellen," p. 340); for example

	Conc. (wt. %)	<i>T.m.d.</i>
Sucrose .....	6.40	+ 0.70°
Glycerol .....	7.40	- 0.78
Methyl alcohol .....	5.00	+ 2.56

Two contributory causes of this action of gelatin on water are immediately obvious. They are, the thermal contraction of the gelatin content of the gel, and the increase in the contraction on imbibition of the gel as a whole (as shown in Table II), with falling temperature.

The thermal contraction of gelatin itself is linear, or nearly so, between 32° and 15°. The increase in the contraction on imbibition of the gel is also linear between these temperatures. If we may assume that both remain linear to temperatures a few degrees below 0°, the temperature of maximum density for different gels can be calculated.

Thus, for a gel containing 13 grams of gelatin per 100 grams of water, or approximately 1 gram of gelatin per 8 grams of water, the volumes containing 1 gram of gelatin are as follow: at 4°, volume of 8 grams of water = 8.00000 c.c.; volume of 1 gram of gelatin = 0.7390 c.c.; contraction = 0.0785 c.c.; volume of gel = 8.66050 c.c.

The similarly calculated values at other temperatures are: 2°, 8.65935 c.c.; 0°, 8.65876 c.c.; - 1°, 8.65868 c.c.; - 2°, 8.65878 c.c.; - 3°, 8.65896 c.c.; - 4°, 8.65930 c.c. Hence the temperature of maximum density for this gel by calculation is - 1.0°. The value found experimentally is - 1.2°. The calculated values for the different gels are summarised in column three of the above table, under "*t.m.d.* calculated."

The agreement between calculation and experiment indicates that the two factors mentioned above are the sole causes of the lowering of the temperature of maximum density of water by gelatin. It throws light, too, on the means by which an externally applied pressure lowers the temperature of maximum density of water. Pressure produces a decrease in the volume of a mass of water, and since the compressibility of water increases with falling temperature, as the temperature is lowered, so the contraction produced by the constant external pressure increases, and this

increasing contraction, that is, decreasing volume, acts against the expansion of the water which begins to take place at  $4^{\circ}$ , and thus lowers the temperature of maximum density by an amount which depends on the pressure applied. That is, the molecules of a mass of water under pressure still undergo that process by which the mass is caused to contract, when cooled, until the temperature is at  $4^{\circ}$ , and then to expand, but the phenomenon is masked and made to appear as though it occurs at a temperature lower than  $4^{\circ}$ .

#### *Summary.*

1. An accurate dilatometer has been described, and a method of filling it with gelatin solution free from air-bubbles.

2. Gelatin gels expand regularly with increasing temperature, the curves of expansion being similar to that of water, but flatter in proportion to the concentration of the gel; the curve shows no sudden change in direction as does glass below its softening point. The coefficients of expansion, and specific volumes for any one temperature, are a linear function of the concentration of the gel. Hydrogen ion does not affect the coefficient of expansion.

3. The contraction resulting on the swelling of gelatin in water is a linear function of the concentration of the gel expressed as grams of gelatin per gram of water at any one temperature, and of the temperature for any one gel. Another way of expressing this is to say that 1 gram of gelatin is always associated with the same contraction in a gel at any one temperature, no matter how much water is contained in the gel; this contraction is 0.073 c.c. per gram of gelatin at  $15.00^{\circ}$ , and 0.065 c.c. at  $32.00^{\circ}$ . This indicates that a fraction only of the water in a gel is contracted, the weight per gram of gelatin undergoing contraction being the same for gels up to at least 25 per cent. concentration by weight. The contraction of a gel is shown not to be due to a filling-up of pores in solid gelatin by water.

4. An explanation has been offered of the curve of double flexure obtained by Sheppard and Sweet for the relationship between concentration and setting point of gelatin gels.

5. The temperatures of maximum density of gelatin gels up to 12 per cent. concentration have been determined. Gelatin lowers the temperature of maximum density of water by an amount directly proportional to its concentration, expressed as grams of gelatin per 100 grams of water. The lowering has been shown to be due to the ordinary volume changes of dry gelatin with changing temperature, and the change in the amount of contraction on imbibition of gels when the temperature varies.

In concluding this paper, I wish to acknowledge my deep indebtedness to Dr. M. W. Travers, at whose suggestion, and under whose guidance, this research was carried out. My best thanks are also due to my professor, F. G. Donnan, for the kind interest which he always showed in this work, and for his helpful criticism; and to Mr. E. Bloom, of Aberdeen University, for the services rendered me during the research.

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### CCXXXVII.—*Diacetylacetone.*

By JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY.

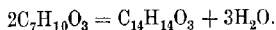
In two former papers (T., 1905, **87**, 1451; 1921, **119**, 1550) it was pointed out that diacetylacetone behaved abnormally both in its chemical and physical properties, if its molecular structure were that represented by the ordinary formula. Since then Morgan and Drew (this vol., p. 928) have found the same with acetylacetone. In the present paper the action of a considerable number of reagents on diacetylacetone has been tried. It does not behave as a triketone, nor as a compound containing ordinary hydroxyl groups. As there are so many possibilities in representing the molecular formula of a compound  $C_7H_{10}O_3$ , all that can be said at present is that the atoms are linked together probably in a ring or rings, and that the open-chain formula for diacetylacetone is inadequate to explain either its properties or reactions.

#### EXPERIMENTAL.

*Diacetylacetone.*—The most convenient method for the preparation of this compound is the following: Dehydracetic acid is boiled with strong hydrochloric acid until the evolution of carbon dioxide ceases. The bulk of the acid is removed by distillation under reduced pressure. The residue is then neutralised with sodium hydroxide, excess of barium hydroxide added, and the mixture just brought to the boiling point. The heavy, yellow precipitate is collected, decomposed with hydrochloric acid, and shaken out with chloroform. The chloroform is distilled off and the residue fractionated under reduced pressure. The diacetylacetone boils without decomposition at  $121^\circ/10$  mm. The distillate does not solidify to a solid mass of crystals for some time. If the refractive index be taken, there is evidence that molecular change occurs. The freshly distilled substance has a refractive

index  $n_D^{20}$  1.4890, it then rapidly changes to 1.4988, when a band forms and darkens, and finally, when the substance crystallises, it becomes constant at 1.4930.

During the preparation of one batch of diacetylacetone, after the diacetylacetone had distilled over, a considerable residue was left in the flask. The residue was dissolved in alcohol, and on cooling a crystalline compound separated. After purification, it melted at 184–185° and was colourless (Found: C = 72.5; H = 6.2.  $C_{14}H_{14}O_3$  requires C = 73.0; H = 6.1 per cent.).



With strong sulphuric acid it gives a deep green colour on warming. With moderately strong sodium hydroxide it gives an insoluble sodium salt; this dissolves on warming, the solution turning yellow. Acids precipitate this solution, giving a lemon-yellow compound, m. p. 125–130°. This yellow compound dissolves in strong sulphuric acid with a red colour. The compound, m. p. 184°, gives no colour with ferric chloride.

Diacetylacetone was treated with the following reagents:

Methyl sulphate gave only dimethylpyrone. With diazomethane, nitrogen was evolved and dimethylpyrone formed. Zinc ethyl in benzene had no action. Benzaldehyde and formaldehyde were without action. Di- and tri-ethylamine, and piperidine gave a yellow naphthalene compound, m. p. 181° ( $C_{14}H_{14}O_3$ ). Benzoyl chloride had no action. Phosphorus pentachloride in chloroform gave dimethylpyrone. Triethylamine in chloroform with iodine gave the compound  $C_7H_7O_3I$  (T., 1921, **119**, 1550).

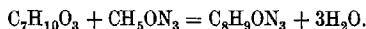
*Phenylhydrazine Compound.*—Phenylhydrazine and diacetylacetone, when warmed together, react with evolution of heat. The resulting compound melts at 142° and is apparently the same compound obtained by Feist from the chloride of dehydracetic acid (Feist, *Annalen*, 1890, **257**, 278) (Found: C = 74.6, 75.2; H = 6.8, 7.0; N = 17.6.  $C_{19}H_{20}N_4$  requires C = 75.0; H = 6.6; N = 18.4 per cent.)



Phenylhydrazine has no action on dimethylpyrone.

*Semicarbazone.*—When diacetylacetone is treated with excess of a slightly alkaline solution of semicarbazide hydrochloride, and left to stand for a day, a crystalline precipitate slowly forms; the crystals continue to separate for over a week. The crystals were dissolved in hot dilute acetic acid. A granular precipitate separated on cooling. The filtrate from the granular precipitate, on standing, gave a further crop of crystals that separated in long, silky needles. These were evidently the chief product of the

reaction. When pure, they melt at 203°. Heated to 100°, they do not lose weight (Found: C = 58.3, 57.8, 57.2; H = 6.1, 6.0, 5.5.  $C_8H_9ON_3$  requires C = 58.8; H = 5.5 per cent.).



The semicarbazone forms salts with both acids and bases.

*Hydrochloride*,  $C_8H_{11}O_2N_3.HCl$ .—When strong hydrochloric acid is added to the semicarbazone a crystalline precipitate is formed. It was recrystallised from alcohol. Its solution in water is acid to litmus paper (Found: in material dried at 100°, C = 43.9; H = 6.1; N = 19.4; Cl = 16.2, 16.6.  $C_8H_{11}O_2N_3.HCl$  requires C = 44.1; H = 5.5; N = 19.3; Cl = 16.3 per cent.). The determination of the chlorine by precipitation with silver nitrate is difficult to carry out, for unless the solution is acid with nitric acid the silver salt of the semicarbazone is precipitated with the silver chloride, and at the same time the nitric acid produces a buff-coloured precipitate that can only be got rid of by prolonged boiling with fuming nitric acid. The hydrochloride is most easily analysed by titration with *N*/10-sodium hydroxide solution. The hydrochloride, when dried at 140°, loses both water and hydrochloric acid, leaving the base  $C_8H_9ON_3$  (Loss found = 24.1.  $C_8H_9ON_3.HCl.H_2O$  requires loss = 25.1 per cent.).

*Sulphate*.—This salt also is not very soluble [Found: in material recrystallised from water and dried at 100°, as  $BaSO_4$ ,  $SO_4 = 21.5$ ; by titration with *N*/10- $NaOH$ ,  $SO_4 = 20.8$ . ( $C_8H_{11}O_2N_3)_2.H_2SO_4$  requires  $SO_4 = 20.8$  per cent.].

*Oxalate*.—This salt also is not very soluble (Found: in material dried at 100°,  $C_2O_4 = 19.8$ .  $C_8H_{11}O_2N_3.H_2C_2O_4$  requires  $C_2O_4 = 19.2$  per cent.).

*Sodium Salt*.—When a strong solution of sodium hydroxide is added to a solution of the semicarbazone the sodium salt is precipitated in silky needles. The solution of the sodium salt is strongly alkaline (Found: Na = 11.9, 12.0, 12.0.  $C_8H_{10}O_2N_3Na$  requires Na = 11.3 per cent.).

*Barium Salt*.—The salt is precipitated by adding a hot solution of barium hydroxide to a solution of the semicarbazone [Found: Ba = 28.0. ( $C_8H_{10}O_2N_3)_2Ba$  requires Ba = 27.6 per cent.]. The semicarbazone dissolves in strong ammonia, but crystallises out on allowing the solution to evaporate. A solution of the semicarbazone gives a white precipitate with silver and mercury salts, but none with those of copper, lead, or iron.

$\frac{1}{2}$  The semicarbazones can be boiled with 90 per cent. sulphuric acid without decomposition. Boiled with strong sodium hydroxide, ammonia is very slowly evolved. Heated with zinc dust in a current of hydrogen, a small quantity of a pyridine base, probably

lutidine, is formed. When a solution of the semicarbazone hydrochloride, cooled in ice, is treated with sodium nitrite, no nitrogen is evolved. But if an excess of nitrous acid be present, the solution turns yellow, and on warming a bright green, crystalline compound separates, having the colour of copper arsenite [Found: in air-dried material,  $C = 42.2$ ;  $H = 6.0$ .  $C_8H_{10}O_2N_3(NO), H_2O$  requires  $C = 42.1$ ;  $H = 5.2$  per cent.]. The air-dried substance, on heating at  $100^\circ$ , loses  $7.5 H_2O$ ; 1 mol.  $H_2O = 7.8$  per cent. [Found:  $C = 46.3$ ;  $H = 4.1$ ;  $N = 26.7$ .  $C_8H_{10}O_2N_3(NO)$  requires  $C = 45.7$ ;  $H = 4.7$ ;  $N = 26.6$  per cent.]. The compound, on heating, does not melt, but suddenly puffs, yielding brown vapours.

The granular precipitate mentioned above in the preparation of the semicarbazone does not seem to be a derivative of diacetylacetone [Found:  $C = 20.7$ ;  $H = 5.0$ ;  $N = 47.6$ .  $(CH_3ON)_2$  requires  $C = 20.3$ ;  $H = 5.1$ ;  $N = 47.4$  per cent.].

The substance is almost entirely insoluble in all organic solvents, but dissolves slightly in boiling water, and more so in hot hydrochloric acid, from which it is precipitated by water. It also dissolves in hot sodium hydroxide, and on boiling there is a slight smell of ammonia. Heated with strong sulphuric acid, carbon dioxide is evolved.

It might be a compound  $(CO \cdot NH \cdot NH_2)_2$ , but all attempts to hydrolyse it and form oxalic acid failed. Also, owing to its great insolubility, attempts to determine its molecular weight were unsuccessful. It is not formed when strong solutions of semicarbazide hydrochloride and sodium hydroxide are left for months.

*Carbamide Compound.*—Diacetylacetone, when heated with carbamide, reacts, and the mixture turns solid. On extracting with alcohol, crystals separate. They are best purified by dissolving in hot hydrochloric acid and precipitating with water, and then melt at  $267$ – $270^\circ$ . They can be sublimed in shining plates (Found:  $C = 56.9$ ;  $H = 5.4$ ;  $N = 8.5$ .  $C_8H_9O_3N$  requires  $C = 57.4$ ;  $H = 5.4$ ;  $N = 8.4$  per cent.).

Hydroxylamine reacts with diacetylacetone, but the resulting compound is a deliquescent liquid and decomposes when heated. It cannot be distilled under reduced pressure, and forms no insoluble or crystalline compounds with either acids or bases. It was therefore not further investigated.

CCXXXVIII.—*Nitro-derivatives of m-Nitrodimethylaniline.*

By AQUILA FORSTER and WILLIAM COULSON.

DURING the preparation and study of 2 : 3 : 4 : 6-tetranitrophenyl-methylnitroamine some nitro-derivatives of 3-nitro-di- and -monomethylanilines have been added to those already described by Romburgh and others. The constitutions of these have been established, and of those prepared by Romburgh confirmed. Some interesting cases of steric hindrance and isomerism have been observed among these compounds.

Romburgh (*Rec. trav. chim.*, 1887, **6**, 253) and Groll (*Ber.*, 1886, **19**, 199) obtained by the nitration of 3-nitrodimethylaniline with nitric acid (*d* 1.2) and also with mixed sulphuric and nitric acids, a mixture of two substances melting at 176° and 112°, respectively, to which Romburgh assigned the constitutions of 3 : 4- and 3 : 6-dinitrodimethylanilines, respectively. He obtained the same mixture by nitrating dimethylaniline dissolved in sulphuric acid with a cold mixture of sulphuric and nitric acids. By the nitration of 3-nitrodimethylaniline with a mixture of dilute sulphuric and nitric acids Swann (*T.*, 1920, **117**, 3) obtained a  $\beta$ -modification, m. p. 154°, of the dinitrodimethylaniline melting at 176° mixed with the dinitrodimethylaniline melting at 112°.

According to Romburgh (*Rec. trav. chim.*, 1889, **8**, 273) the dinitrodimethylaniline melting at 176° (3 : 4), when dissolved in nitric acid (*d* 1.36), gave a mixture of two trinitrodimethylanilines, m. p. 154° and 196°, respectively, whereas the dinitrodimethylaniline melting at 112° gave only one trinitrodimethylaniline, m. p. 196°. The latter trinitrodimethylaniline was also obtained by Swann (*loc. cit.*) by nitrating the  $\beta$ -dinitrodimethylaniline melting at 154° with 70 per cent. nitric acid.

3-Nitrodimethylaniline has been found to nitrate readily with 70 per cent. nitric acid to a mixture of the trinitrodimethylaniline, m. p. 196°, already described by Romburgh, and a substance melting at 138°. This substance has been shown to be 2 : 3 : 6-trinitrodimethylaniline\* by conversion into 4-bromo-2 : 6-dinitro-1 : 3-di(methylnitroamino)benzene (X), and by its decomposition by means of aqueous sodium hydroxide solution into dimethylamine (converted by means of picryl chloride into dimethylpicramide) and 2 : 6-dinitro-1 : 3-dihydroxybenzene.

\* The substance mentioned by Blanksma (*Rec. trav. chim.*, 1902, **21**, 266) as 2 : 3 : 6-trinitrodimethylaniline with reference to Romburgh (*ibid.*, 1889, **8**, 274) is 2 : 3 : 4-trinitrodimethylaniline.

The isolation of 2:3:6-trinitrodimethylaniline determines by elimination the constitutions of the unsymmetric nitro-di- and mono-methylanilines. There are three trinitrodimethylanilines derived from 3-nitrodimethylaniline now known, melting at 154°, 197°, and 138°, respectively. The substance melting at 197° was oxidised by Swann to 3:4:6-trinitromonomethylaniline (VIII), the constitution of which he determined by conversion into the corresponding anisidine. This conclusion has now been confirmed by heating the oxidation product with dilute sodium hydroxide solution, when monomethylamine (converted into monomethylpicramide), and 4:6-dinitro-1:3-dihydroxybenzene, m. p. 235°, were obtained. Hence the substance melting at 197° is 3:4:6-trinitrodimethylaniline (V).

The substance melting at 154° may now be the 2:3:4- or the 3:4:5-trinitrodimethylaniline. Romburgh, however, converted it by means of methylamine into a substance which nitrated to 2:4:6-trinitro-1:3-di(methylnitroamino)benzene, thus proving its constitution as 2:3:4-trinitrodimethylaniline (IV).

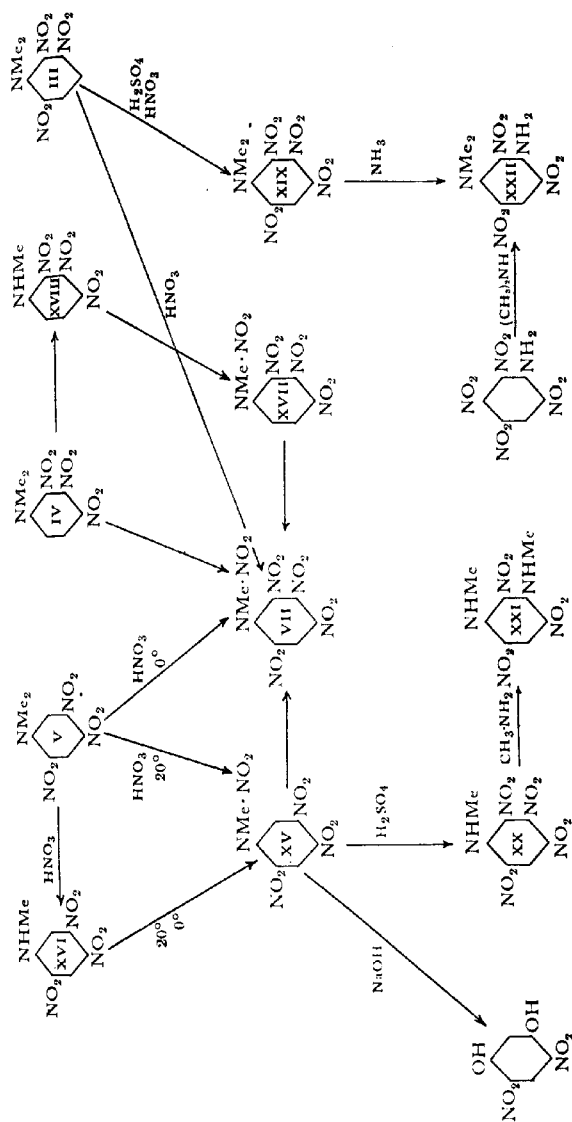
Further, together with 2:3:6- and 3:4:6-trinitrodimethylanilines it gives with boiling nitric acid 2:3:4:6-tetranitrophenylmethylnitroamine, m. p. 145° (VII), the 5-position in which must therefore be vacant, no pentanitrophenylmethylnitroamine (m. p. 132°) being obtained.

Only two dinitrodimethylanilines are known, melting at 112° and 176°, neither being the 3:5-dinitrodimethylaniline which, although not isolated, is stated by Blanksma (*Rec. trav. chim.*, 1902, 21, 266) to nitrate to pentanitrophenylmethylnitroamine, m. p. 132°. The substance melting at 176° cannot have the para-position open, because in that case one of its trinitro-derivatives would be 2:3:6-trinitrodimethylaniline; by nitration, however, it gives a mixture of 3:4:6-trinitrodimethylaniline (m. p. 196°) (V) and the trinitrodimethylaniline melting at 154°. Hence it is the 3:4-dinitrodimethylaniline (I). The substance melting at 112° gives by nitration only the 3:4:6-trinitrodimethylaniline; further, it has now been converted by bromination and nitration into 4-bromo-2:3:6-trinitrophenylmethylnitroamine, m. p. 165° (XII), proving the (para) 4-position to be vacant. Hence it is the 3:6-dinitrodimethylaniline (II).

2:3:6-Trinitrodimethylaniline and one molecule of nitric acid gave a substance melting at 153°. Cold aqueous ammonia converted this into a substance melting at 187°, shown to be 3-aminodimethylpicramide (XXII) by its preparation from cold aqueous dimethylamine and 2:3:4:6-tetranitroaniline, and by its nitration to 2:4:6-trinitro-3-hydroxyphenylmethylnitroamine (2:3:4:6-







tetranitroaniline and monomethylamine gave 2:4:6-trinitro-3-aminomonomethylaniline, m. p. 190°. The substance melting at 153° is therefore 2:3:4:6-tetranitrodimethylaniline (XIX). Boiling nitric acid converted it into 2:3:4:6-tetranitrophenylmethylnitroamine.

3:4:6-Trinitromonomethylaniline (XVI) has now been found to nitrate in nitric acid to a substance melting at 143.5°. This substance was converted by means of sodium hydroxide solution into 4:6-dinitro-1:3-dihydroxybenzene, and by sulphuric acid into a substance melting at 127°. The latter substance gave with cold aqueous monomethylamine 2:4:6-trinitro-1:3-di(monomethylamino)benzene, m. p. 235° (XXI), and therefore is 2:3:4:6-tetranitromonomethylaniline (XX). Hence the substance melting at 143.5° is 3:4:6-trinitrophenylmethylnitroamine (XV).

3:4:6-Trinitrophenylmethylnitroamine is a white, crystalline solid, stable in nitric acid, from which it crystallises in hard, white needles. Boiling 90 per cent. nitric acid only slowly nitrated it to 2:3:4:6-tetranitrophenylmethylnitroamine (VII) (m. p. 147°; crystallised from nitric acid). Aqueous ammonia gave 4:6-dinitro-3-aminophenylmethylnitroamine, m. p. 169°. One molecule of potassium hydroxide in boiling alcohol converted it into 4:6-dinitro-3-ethoxyphenylmethylnitroamine, m. p. 135.5°, which with alcoholic monomethylamine gave 4:6-dinitro-3-monomethylaminophenylmethylnitroamine, melting at 181.5° and nitrating in boiling 90 per cent. nitric acid to 2:4:6-trinitro-1:3-di(methylamino)benzene, m. p. 206°. Cold acetone rapidly decomposed it.

Similarly, 2:3:4-trinitromonomethylaniline (XVIII) has been found to nitrate to a substance melting at 122.5°, which was shown to be 2:3:4-trinitrophenylmethylnitroamine (XVII) by its conversion by means of sodium hydroxide solution into 2:4-dinitro-1:3-dihydroxybenzene, m. p. 167°. Boiling 90 per cent. nitric acid only slowly nitrated it to the tetranitro-nitroamine.

#### *Steric Hindrance.*

The positions occupied by nitro-groups during the nitration of 3-nitrodimethylaniline and its derivatives appear to be largely controlled by steric hindrance.

Thus all attempts to prepare 2:3-dinitrodimethylaniline by nitrating 3-nitrodimethylaniline gave only 3:4- and 3:6-dinitrodimethylanilines. Further, 3:6-dinitrodimethylaniline was recrystallised unchanged from 70 per cent. nitric acid at 40°, in which 3:4-dinitrodimethylaniline readily nitrated to give 3:4:6-trinitrodimethylaniline mixed with a little 2:3:4-trinitrodimethylaniline (at 60° to 70°, it gave pure 3:4:6-trinitrodimethylaniline).

There was evidence, however, that 2:3-dinitrodimethylaniline was formed during the nitration of 3-nitrodimethylaniline with a stronger and less selective acid, such as 70 per cent. nitric acid at 40°, when 2:3:6-trinitrodimethylaniline mixed with 3:4:6-trinitrodimethylaniline was obtained. As shown above, this substance could not have been formed under these conditions from 3:6-dinitrodimethylaniline, but was presumably derived from the intermediate 2:3-dinitrodimethylaniline.

Steric hindrance again appeared to play an importance rôle in the nitration of the trinitrodimethylanilines, resisting the entrance of a nitro-group in the ortho-position between a methylnitroamino-group and a *m*-nitro-group, or even adjacent to a methylnitroamino-group alone. This has already been indicated in the resistance to further nitration in hot 70 per cent. nitric acid of 3:4:6- and 2:3:4-trinitrophenylmethylnitroamines. It was fully shown in the nitration of 3:4:6-trinitrodimethylaniline (V). This substance, when dissolved in 90 per cent. nitric acid at 0°, was converted quantitatively into pure 2:3:4:6-tetranitrophenylmethylnitroamine, m. p. 147° (VII); but when this solution was made at 20° instead of at 0°, a mixture melting at 104–106°\* and consisting of 3:4:6-trinitrophenylmethylnitroamine (XV) and 2:3:4:6-tetranitrophenylmethylnitroamine was obtained. This mixture remained unchanged in 90 per cent. nitric acid at 60°; boiling 90 per cent. nitric acid, containing a little sulphuric acid, slowly nitrated the 3:4:6-trinitrophenylmethylnitroamine to 2:3:4:6-tetranitrophenylmethylnitroamine, and after several hours converted the mixture into the latter substance, m. p. 147°.

This indicated that when the dimethylamino-group had been converted into a methylnitroamino-group by oxidation and nitration before the ortho-position adjacent to the *m*-nitro-group had been filled, the ortho-position was sufficiently protected to prevent the entrance of a nitro-group except by comparatively drastic means. At low temperatures, the conversion of the dimethylamino-group into a methylnitroamino-group appeared to take place slowly, allowing the ortho-positions to be previously nitrated; at the ordinary temperature and above, some methylnitroamino-nitration occurred before the ortho-position was occupied, the latter being then protected. Confirming this explanation, 2:3:6-trinitrodi-

\* This mixture could not be fractionated by crystallisation from nitric acid, but was converted by alcohol and sodium hydroxide solution into a mixture of 4:6-dinitro-3-ethoxyphenylmethylnitroamine, m. p. 135.5°, and 2:4:6-trinitro-3-ethoxyphenylmethylnitroamine, m. p. 98°, the constituents of which were separated by crystallisation from alcohol and identified. These phenetoles gave with alcoholic methylamine the corresponding nitromethylaminonitroamines, melting at 181.5° and 192°, respectively.

methylaniline, in which the adjacent ortho-positions are occupied, when dissolved in 90 per cent. nitric acid at 20°, gave a quantitative yield of 2:3:4:6-tetranitrophenylmethylnitroamine, m. p. 147°.

The oxidation of 3:4:6-trinitrodimethylaniline (V) to 3:4:6-trinitromonomethylaniline (XVI) by 70 per cent. nitric acid at high temperatures without further nitration (Swann, *loc. cit.*, supports this view. Further agreement was obtained from the nitration of 3:4:6-trinitromonomethylaniline (XVI), which gave at 0° and at 20° quantitative yields of 3:4:6-trinitrophenylmethyl-nitroamine, m. p. 143.5° (XV).

2:3:4-Trinitrodimethylaniline (IV) in nitric acid gave in each case quantitative yields of 2:3:4:6-tetranitrophenylmethyl-nitroamine. It would appear that nitration in the 6-position of 2:3:4-trinitrodimethylaniline was complete before oxidation of the dimethylamino-group, even at high temperatures, and that steric hindrance in the absence of an adjacent *m*-nitro-group was less than in the case of 3:4:6-trinitrodimethylaniline. As already described, 2:3:4-trinitromonomethylaniline nitrated first to 2:3:4-trinitrophenylmethylnitroamine, after which the methyl-nitroamino-group evidently protected the 6-position, even in the absence of an adjacent *m*-nitro-group, sufficiently to prevent its occupation by a nitro-group except by drastic means.

#### Oxidation.

By the action of hot dilute nitric acid on 3:4:6-trinitrodimethylaniline, Swann (*loc. cit.*) removed one of the methyl groups by oxidation and obtained 3:4:6-trinitromonomethylaniline, m. p. 199°. This oxidation has been applied to 2:3:6- and 2:3:4-trinitrodimethylanilines. The former gave only phenolic substances; from the latter a good yield of 2:3:4-trinitromonomethylaniline was obtained identical with the product obtained by Romburgh by the oxidation of 2:3:4-trinitrodimethylaniline with chromic acid.

Romburgh oxidised 3:6-dinitrodimethylaniline with chromic acid to 3:6-dinitromonomethylaniline, m. p. 166°. This oxidation, applied to 3:4-dinitrodimethylaniline, was found to give 3:4-dinitromonomethylaniline, m. p. 156°; with boiling 20 per cent. nitric acid an orange compound melting at 166° (unchanged from sulphuric acid) was obtained.

#### Bromination.

Bromine water added to 3-nitrodimethylaniline dissolved in dilute hydrochloric acid precipitated a substance melting at

95°, which was shown to be 4-bromo-3-nitrodimethylaniline\* (XI) by its quantitative preparation by the cold nitration of 4-bromodimethylaniline, m. p. 55°. 4-Bromo-3-nitrodimethylaniline was nitrated to 4-bromo-2:3:6-trinitrodimethylaniline (scarlet), m. p. 167°, which by further nitration yielded a white nitroamine, 4-bromo-2:3:6-trinitrophenylmethylnitroamine (XII), m. p. 165°. The constitution of this substance was proved by its reaction with monomethylamine to give 4-bromo-2:6-dinitro-3-methylamino-phenylmethylnitroamine (XIII), m. p. 176°, formerly prepared from 3:4-dibromo-2:6-dinitrophenylmethylnitroamine (XIV) by Blanksma (*Rec. trav. chim.*, 1902, **21**, 415), and which by further nitration gave 4-bromo-2:6-dinitro-1:3-di(methylnitroamino)-benzene (X), m. p. 174° with decomposition (Blanksma, *loc. cit.*).

3:6- and 3:4-Dinitrodimethylaniline were found to brominate readily, giving 4-bromo-3:6-dinitrodimethylaniline, scarlet form, m. p. 108°, orange form, m. p. 174°; and 6-bromo-3:4-dinitrodimethylaniline, scarlet form, m. p. 119°, orange form, m. p. 131°, respectively. These compounds appeared to exist in a number of chromoisomeric forms, of which only two were examined. By nitration, they gave the corresponding nitroamines, 4-bromo-2:3:6-trinitrophenylmethylnitroamine, m. p. 165°, identified with that prepared from 3-nitrodimethylaniline, and 6-bromo-2:3:4-trinitrophenylmethylnitroamine, m. p. 116°, respectively.

Attempts to brominate 2:3:6-trinitrodimethylaniline left it unchanged, the para-position apparently being protected. After replacing the 3-nitro-group by monomethylamine, giving 2:6-dinitro-3-methylaminodimethylaniline (VI), m. p. 119°, bromination took place readily, giving 4-bromo-2:6-dinitro-3-methylaminodimethylaniline (IX) melting at 114°, which by nitration yielded a nitroamine, m. p. 174°, identified with 4-bromo-2:6-dinitro-1:3-di(methylnitroamino)benzene (X) obtained as described above from 4-bromo-3-nitrodimethylaniline.

#### *Substitution of the m-Nitro-group.*

Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1034) observed the reactivity of the *m*-nitro-group in 2:3:4- and 3:4:6-trinitrodimethylaniline and in 2:3:4:6-tetranitrophenylmethylnitroamine, substituted for it amino- or alkylamino-groups, and prepared a number of derivatives. Similarly, Swann (*loc. cit.*) prepared an anisidine from 3:4:6-trinitromonomethylaniline.

The 3-nitro-group in 3:4-dinitrodimethylaniline has been found

\* Identified with the substance melting at 94° described by Ephraim and Hochuli (*Ber.*, 1915, **48**, 360). The substance, m. p. 72°, described by Koch (*Ber.*, 1887, **20**, 2961) as 4-bromo-3-nitrodimethylaniline is 4-bromo-2-nitrodimethylaniline (*vide* Pinnow, *Ber.*, 1898, **31**, 2984).

to be mobile, but less so than that in the trinitrodimethylanilines, with monomethylamine, the dinitrodimethylaniline gave 4-nitro-3-monomethylaminodimethylaniline, m. p.  $117^{\circ}$ . This product nitrated quantitatively in nitric acid to 2:4:6-trinitro-1:3-di(methylnitroamino)benzene, m. p.  $206^{\circ}$ .

2:3:6-Trinitrodimethylaniline, in which the 3-nitro-group has been found to be similarly mobile, gives with aqueous sodium hydroxide solution 2:6-dinitro-3-hydroxydimethylaniline, m. p.  $191^{\circ}$ ; with aqueous ammonia 2:6-dinitro-3-aminodimethylaniline, m. p.  $160^{\circ}$ ; with aqueous monomethylamine 2:6-dinitro-3-monomethylaminodimethylaniline, m. p.  $121^{\circ}$ ; and with alcoholic aniline 2:6-dinitro-3-anilindimethylaniline, m. p.  $135^{\circ}$ .

Similarly, the *m*-nitro-group in the 2:3:4:6-tetranitromethylanilines was found to react readily in the cold. Thus 2:3:4:6-tetranitrodimethylaniline (XIX) gave with cold aqueous ammonia 2:4:6-trinitro-3-aminodimethylaniline (XXII), m. p.  $187^{\circ}$ , and 2:3:4:6-tetranitromonomethylaniline (XX) (from 3:4:6-trinitrophenylmethylnitroamine and sulphuric acid) with aqueous monomethylamine gave 2:4:6-trinitro-1:3-di(monomethylamino)benzene (XXI), m. p.  $130^{\circ}$ .

The conversion of the amino- to a nitroamino-group increased the mobility of the *m*-nitro-group. Whereas all the nitro-di- and -mono-methylanilines were found to be stable in boiling water and neutral solvents, the nitroamines prepared from them decomposed rapidly in hot water, in cold alcohol, and in acetone. Thus, for instance, a marked distinction in properties was found between 2:3:4:6-tetranitromonomethylaniline (also 2:3:4:6-tetranitrodimethylaniline) and the isomeric 3:4:6-trinitrophenylmethylnitroamine (compare also van Duin, *Rec. trav. chim.*, 1920, **39**, 145).

4-Bromo-2:3:6-trinitrodimethylaniline (*vide supra*) was found to be remarkably stable; the *m*-nitro-group, evidently protected by the bromine, was not attacked by methylamine or ammonia. The introduction of a nitroamino-group, however, rendered the *m*-nitro-group reactive, and several derivatives were prepared.

#### *Chromoisomerism.*

Chromoisomerides excepting nitroamines appear to consist in red and yellow or orange modifications, of which the latter usually have the higher melting points. They all, however deeply coloured, give colourless solutions in sulphuric, nitric, or acetic acid. The yellow form is obtained as a rule from dehydrating acids, and the red modification in the presence of aqueous solvents or aqueous acids. Thus in some cases, when a concentrated solution of the nitroaniline in sulphuric acid is gradually diluted with water

to the point of precipitation, the yellow form appears, but when the solution is poured into a large excess of water the red form may be obtained. In the case of 3 : 6-dinitrodimethylaniline, which is red, a yellow modification was precipitated by cooling a warm saturated solution in acetic acid saturated with hydrogen chloride gas; when isolated, however, it rapidly reverted to the red form.

Chromoisomerides appear to be more prevalent among the nitro- and bromonitro-dimethylanilines than among the corresponding monomethylanilines.

3 : 6-Dinitrodimethylaniline, (*a*) scarlet, *m.* p. 112°, from alcohol and from nitric or acetic acid; (*b*) orange to yellow, unstable, obtained by adding hydrogen chloride to a saturated solution in glacial acetic acid.

4-Bromo-3 : 6-dinitrodimethylaniline, (*a*) scarlet, *m.* p. 108°, from alcohol containing hydrogen bromide, or from nitric acid by dilution; (*b*) light yellow, *m.* p. 174°, from alcohol and from sulphuric or acetic acid by precipitation with water.

6-Bromo-3 : 4-dinitrodimethylaniline, (*a*) scarlet, *m.* p. 119°, from alcohol; (*b*) yellow, *m.* p. 131°, from acetic acid.

2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine, (*a*) white, *m.* p. 186°, from nitric acid; (*b*) lemon yellow, *m.* p. 175°, from water.

*Homochromoisomerism*.—3 : 4 : 6-Trinitromonomethylaniline, lemon yellow, (*a*) *m.* p. 201°, from acetone; (*b*) *m.* p. 132°, from nitric acid.

*Isochromoisomerism*.—3 : 4 : 6-Trinitrodimethylaniline, *m.* p. 198°, (*a*) orange-red, from acetone; (*b*) lemon-yellow, from sulphuric acid by precipitation with water.

3-Nitrodimethylaniline, *m.* p. 57°, from (*a*) orange-yellow to (*b*) deep red.

2 : 4 : 6-Trinitrophenylmethylnitroamine, *m.* p. 128—129°, (*a*) white, from nitric acid; (*b*) yellow, after fusion.

2 : 4 : 6-Trinitrophenylethylnitroamine, *m.* p. 95°, (*a*) white, from nitric acid; (*b*) deep yellow, after fusion.

4-Bromo-2 : 4 : 6-trinitro-3-methylaminodimethylaniline, *m.* p. 114°, (*a*) orange, from alcohol; (*b*) red, from acetic acid.

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CCXXXIX.—*Preparation and Reactions of Stannous Oxide and Stannous Hydroxides.\**

By FRANK WARD BURY and JAMES RIDDICK PARTINGTON.

DITTE (*Ann. Chim. Phys.*, 1882, [v], 27, 145) prepared stannous hydroxide by adding sodium or potassium hydroxide to a solution of stannous chloride, the precipitate being washed by decantation and dried in a vacuum at 14°. He obtained a brownish-yellow, amorphous powder to which he assigned the formula  $\text{SnO}, 2\text{H}_2\text{O}$ . On heating this powder at 110°, Ditte obtained small, brown scales which could be readily powdered. To this substance he assigned the formula  $3\text{SnO}, 2\text{H}_2\text{O}$ . Ditte does not mention the methods used in analysing the substances.

Schaffner (*Annalen*, 1844, 51, 168) prepared a specimen of stannous hydroxide by the addition of potassium carbonate to stannous chloride solution. He dried the precipitate below 80°. The amount of water in the compound was estimated by heating it to dull redness in a bulb tube in a stream of carbon dioxide, and assuming the loss in weight to be water and the residue stannous oxide. No estimation of the percentage of tin present in the compound was made. Schaffner assigned to this compound the formula  $2\text{SnO}, \text{H}_2\text{O}$ . He described the precipitate produced by the addition of ammonia to stannous chloride as "a basic salt."

In view of the discrepancies between these statements, the matter was thought worthy of re-investigation. Specimens of stannous hydroxides were prepared by methods described by previous investigators and analysed.

EXPERIMENTAL.

*Preparation of the Specimens of Stannous Hydroxide.*

The stannous chloride solution was made by adding 22.5 grams of crystalline stannous chloride to 100 c.c. of water. This solution was clarified by addition of a minimum amount of strong hydrochloric acid and tin and heating. The calculated amount of precipitant was used, as it was noted that excess of alkali caused the stannous hydroxide to darken and become almost black.

*Sample A.*—To the solution of stannous chloride, sodium hydroxide solution was added until a faint permanent precipitate was produced. The calculated amount of sodium hydroxide (8 grams)

\* "Stannous hydroxide" throughout this paper means a hydrated form of stannous oxide obtained by any method described, and not necessarily the definite compound  $\text{Sn}(\text{OH})_2$ ; perhaps a more suitable name would be "hydrated stannous oxide" or "stannous oxide hydrate."

necessary for precipitation was then added. There is therefore a slight excess of stannous chloride in this solution. The precipitate was washed with cold boiled water in a Büchner funnel. No precautions were taken to prevent access of air. The precipitate was distinctly yellow, very gelatinous, and obviously colloidal. After drying in a desiccator over calcium chloride for two days, it was, when powdered, distinctly yellow and readily soluble in dilute hydrochloric acid; the solution gave a copious precipitate with mercuric chloride. The powder was placed in a vacuum desiccator over phosphoric oxide for fourteen days and then analysed.

*Sample B.*—To the solution of stannous chloride made as in the preparation of sample *A* a very concentrated sodium carbonate solution was added until a faint precipitate was produced. To this solution, 10.6 grams of pure anhydrous sodium carbonate were added, the liquid was filtered, and the precipitate washed with boiled water. This precipitate tended to pass through the filter. It was dried in a desiccator over calcium chloride for four days, then powdered, and placed in a vacuum desiccator during the vacation for one month, but at the end of the time the vacuum had disappeared. The sample was placed in an atmospheric desiccator over calcium chloride, phosphoric oxide, and potassium hydroxide for a further fourteen days and then analysed.

*Sample C.*—To the stannous chloride solution prepared as in *A*, neutralised with sodium carbonate, enough ammonia was added to give a faint smell of ammonia, and the precipitate was washed as before. The sample was left in a desiccator over phosphoric oxide.

*Sample F.*—According to Roscoe and Schorlemmer ("Treatise," 1913, Vol. II, p. 854) stannous hydroxide is rapidly oxidised by the air. Sample *F* was prepared in a similar way to sample *C*, but precautions were taken to exclude air and to carry out the preparation in an atmosphere of carbon dioxide.

The stannous hydroxide was precipitated in a flask filled with boiled water and filtered in a Büchner funnel arranged with a brass cover with three tubulures. Through two of these a stream of carbon dioxide was kept passing. Through the third passed a siphon tube from the flask containing the precipitate, the liquid being displaced into the funnel by a stream of carbon dioxide admitted through a second tube in the cork of the flask. This flask was afterwards filled through the second tube with boiled water, which was used for washing the precipitate.

*Sample H* was prepared by means of the apparatus described in the preparation of *F*, but using the calculated amount of sodium carbonate as the precipitant. The stannous hydroxide was placed

in a vacuum desiccator containing phosphoric oxide for fourteen days before analysis.

*Appearance of the Specimens A, B, C, F, and H.*—Samples *A*, *B*, and *H* had a yellow tinge when first precipitated, which became more marked on drying. Samples *C* and *F*, prepared by precipitating with ammonia, were white at first, but became yellow on drying. On keeping them in glass specimen tubes, they became darker on the outside, that is, the parts touching the glass. Ditte comments on this phenomenon and states that the parts of the dried specimens in contact with the glass go brown owing to their "containing less water than the original hydrate," but does not state how he drew this conclusion. It has already been mentioned that an excess of alkali darkens the stannous hydroxide, so that this change of colour may be due to traces of alkali on the glass. This explanation was confirmed by keeping the specimens in silica tubes, when no change of colour was observed. Specimens *A*, *B*, *C*, *F*, and *H* were all amorphous and colloidal towards the end of the washing and had a tendency to pass through the filter-paper. They were readily soluble in cold dilute hydrochloric acid, indicating the absence of stannic oxide. On boiling portions of the specimens with dilute nitric acid and adding silver nitrate, a slight opalescence was obtained, showing that the chloride had not been entirely removed.

*Preparation of Samples D, E, and G.*—In the preparation of these samples, *D* by precipitation with sodium hydroxide, *E* and *G* by precipitation with sodium carbonate, the stannous hydroxide began to pass through the Büchner filter before the precipitates were free from chloride. They were therefore mixed together and the washing continued by decantation. The flasks were arranged as wash-bottles. The solutions containing the suspended stannous hydroxide entirely filled the flasks. When the stannous hydroxide had settled down, the liquid was decanted by attaching a Kipp's apparatus, generating carbon dioxide, to the tube not acting as the syphon. The precipitate slowly became dark grey. It was left under water for several weeks in a corked flask filled with water. The walls of the flask became covered with small clusters of needle-shaped crystals in about five weeks' time, dark in appearance, with a silvery lustre. On addition of water, many similar although smaller crystals were in suspension, and gave a creamy, yellow liquid which glistened on shaking. The black solid, on treatment with water, gave a similar solution. It filtered very slowly. A little ammonium chloride solution was added, and on warming, a yellow, flocculent precipitate, which readily filtered, was obtained. We may regard the yellow solution as a

colloidal solution of crystalline stannous oxide. The precipitate was filtered off, washed, and dried in a steam-oven.

The black residue remaining in the flask was the same product as that obtained above, as on the addition of water it gave the same olive-green paste, which on further addition of water became a creamy, yellow liquid, which glistened on shaking.

A weighed portion of the mixed samples *D, E, G*, was dried in an air-oven at  $110^{\circ}$  and cooled in a desiccator.

#### *Analyses of All Samples.*

The percentage of tin was estimated by igniting the sample in a porcelain crucible and assuming the residue to be  $\text{SnO}_2$ .

The percentage of water was estimated by finding the loss in weight on heating in an atmosphere of carbon dioxide in a bulb tube (Schaffner, *Annalen*, 1844, **51**, 168). In each case there was a little sublimate produced, which dissolved readily in water and gave a black coloration with silver nitrate and a slight precipitate with mercuric chloride, indicating that the sublimate was stannous chloride. This sublimate was driven off and the tube again weighed. The loss was never more than 0.2 per cent., and in most cases was negligible.

The chloride present was also estimated by fusing a weighed portion of the sample with sodium carbonate. The residue was boiled with water and filtered. To the filtrate 10 c.c. of  $N/10$ -silver nitrate solution were added and the excess was estimated by titration with  $N/10$ -potassium thiocyanate with iron alum as indicator.

In samples *A, B, C, F*, and *H*, the chloride present was negligible. In sample (*D, E, G*) the chlorine found corresponded with 0.979 per cent. of stannous chloride.

The results are tabulated below :

	% Sn.	% $\text{H}_2\text{O}$ .	% O by calculation as $\text{SnO}$ .
<i>A</i>	80.9	7.11	10.86
<i>B</i>	79.82	8.54	10.72
<i>C</i>	79.41	8.32	10.67
<i>F</i>	80.5	8.82	10.8
<i>H</i>	80.91	7.4	10.86

Results with (*D, E, G*) after heating in an air-oven at  $110^{\circ}$ : Percentage of  $\text{SnO}$  found was 95.76;  $\text{H}_2\text{O}$ , 2.5;  $\text{SnCl}_2$ , 0.979.

The percentage of  $\text{SnO}$  found in this sample after heating in an air-oven at  $160^{\circ}$  for two and three-quarter hours was 94.62. Thus the oxidation had become marked.

*Conclusions.*

- (1) The six samples were essentially the same.
- (2) Little or no reaction occurs between moist stannous hydroxide and the atmosphere at the ordinary temperature.
- (3) The precipitate with ammonia is probably the same as the others, although Schaffner states this to be a basic salt.

Fremy (*Ann. Chim. Phys.*, 1844, [iii], **12**, 460) describes a reddish-brown stannous oxide obtained on precipitating stannous chloride with a slight excess of ammonia and boiling for some time. Attempts to obtain this variety were unsuccessful. In one case only, a slight red tinge appeared on the glass where part of the liquid had dried, but the solid in suspension did not become red.

- (4) No sample was entirely free from chlorine, although in most cases the amount was negligible.

## (5) Probable formula :

		% Sn.	% H <sub>2</sub> O.	% O.
Schaffner	2SnO. <sub>2</sub> H <sub>2</sub> O requires .....	82.64	6.25	11.11
"	obtained .....		6.46	
Ditte	3SnO. <sub>2</sub> 2H <sub>2</sub> O requires .....	80.97	8.16	10.87
"	obtained (?).....	79.13	8.87	11.11

Ditte does not in any single case give his experimental methods, but states that the specimen was obtained in "brownish scales" by drying the precipitated hydroxide at 110°. He assigns the formula SnO.<sub>2</sub>2H<sub>2</sub>O to a brownish-yellow, amorphous powder obtained by leaving the hydrate in a vacuum at 14°.

The analyses of samples *A*, *B*, *C*, *F*, and *H* support the formula 3SnO.<sub>2</sub>2H<sub>2</sub>O.

- (6) The result with (*D*, *E*, *G*) indicates that stannous hydroxide is stable at 110°; the percentage of water then fell to 2.5. The 0.8 per cent. unaccounted for may be due to some oxidation.

(7) Stannous hydroxide, on standing under water, slowly loses water to become stannous oxide.

- (8) Stannous hydroxide does not lose the whole of its water at 160°. In all probability some of the water is constitutional.

*Supposed Modification of Stannous Oxide.*

Ditte describes a number of experiments with stannous hydroxide in which several varieties of stannous oxide, differing in appearance, colour, and density, were produced.

For an account of these, reference must be made to the original paper, but it may be stated that the experimental conditions are not clearly described by Ditte. In many cases it was found impossible to confirm the statements of the latter. It will be sufficient to give a brief account of the results obtained, which may be compared with those described by Ditte.

(1) *Reaction with Stannous Chloride.*—The dried specimens of the hydroxide were boiled with water and one or two crystals of stannous chloride: a faint salmon-pink suspension was obtained, which did not darken further on boiling. On the addition of excess of stannous chloride, the stannous hydroxide became white again. There was no red, green, or black colour produced, as stated by Ditte.

A sample of stannous hydroxide was prepared as in sample *B*, but *not dried*. It was kept under water and slowly became black on the outside when exposed to light. This stannous hydroxide is referred to as "wet stannous hydroxide." To about 1 gram of the wet stannous hydroxide suspended in cold water, two or three crystals of stannous chloride were added. The hydroxide slowly became grey on heating, but no red colour was seen; an olive-green oxide slowly precipitated after five minutes, but a good deal of white stannous hydroxide was left.

(2) *Reaction with Hydrochloric Acid.*—No change was observed on boiling the dry or wet stannous hydroxide with very dilute hydrochloric acid.

(3) *Reaction with Ammonium Chloride Solution of Various Strengths.*—On boiling the stannous hydroxide with solutions of ammonium chloride of various strengths, Ditte obtained several modifications of stannous oxide.

These experiments were repeated with the dried specimens. No change was observed on boiling them with the ammonium chloride solutions. There was a slight change observed when the wet stannous hydroxide was used, but the amount of ammonium chloride present appeared to have no effect on the result. On boiling with the ammonium chloride solution, the stannous hydroxide slowly became grey, and a dark grey, sandy, crystalline precipitate of stannous oxide was formed in all cases. The precipitate, on washing with water, gave a milky liquid.

The product in all experiments always appears to be the same, namely, the dark grey stannous oxide which is formed slowly when the white hydroxide is kept under water. The white hydroxide appears to be an unstable substance which slowly decomposes into stannous oxide, and the various reagents described by Ditte appear to act catalytically in accelerating this change.

(4) *Reactions with Acetic Acid.*—The wet stannous hydroxide was dissolved in acetic acid solution (10 c.c. of glacial acetic acid diluted to 85 c.c.).<sup>\*</sup> The excess of stannous hydroxide was filtered off and the filtrate transferred to a desiccator containing concentrated sulphuric acid and potassium hydroxide. In two months, a yellow, crystalline solid was obtained. This solid, on ignition,

blackened, and then became yellow; the residue, on cooling, was nearly white. Assuming the residue to be stannic oxide, the percentage of tin found in the substance was 49.55. The percentage of tin required by the formula  $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$  is 50.1. This substance is probably stannous acetate containing a little water. It is rather hazardous to assign the percentage of tin to Ditte's formula,  $2(\text{C}_4\text{H}_3\text{O}_3)\text{SnO}\cdot\text{HO}\cdot 2\text{H}_2\text{O}$ , for this substance, as he does not state what atomic weights he used, and appears to use  $\text{H}$  and  $\text{H}_2\text{O}$  indiscriminately for the formula of water.

To the wet stannous hydroxide in boiling water a few drops of glacial acetic acid were added. There was a darkening of colour, and a black precipitate was produced, but the liquid retained its yellow tint. With excess of glacial acetic acid, the precipitate became yellowish-white.

It was not found possible to prepare the red form obtained by Roth (Abegg, III, 2, 573) by heating the hydroxide with a solution of stannous oxide in acetic acid.

(5) *Reaction with Nitric Acid*.—On treating wet stannous hydroxide with dilute nitric acid, a solution was obtained. This was left in the desiccator for two months; a solid residue of a white, porcelain-like appearance remained. On ignition, white and then brown fumes were evolved, and assuming the residue to be stannic oxide, the percentage of tin contained in this substance was found to be 55.4. The substance did not detonate on heating. The compound was insoluble in cold water and not completely soluble in hot water, gave no precipitate with mercuric chloride, and is probably a basic stannic nitrate.

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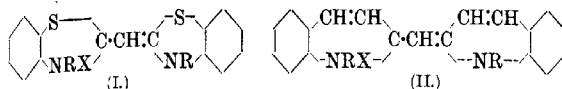
[Received, July 4th, 1922.]

CCXL.—*The Cyanine Dyes. Part VI. Dyes containing a Quinoline and a Benzothiazole Nucleus The Thioisocyanines.*

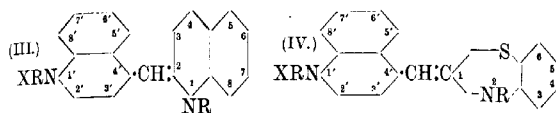
By WALTER THEODORE KARL BRAUNHOLTZ and WILLIAM HOBSON MILLS.

A SERIES of yellow photosensitising dyes, the thiocyanines, have recently been described by one of us (Mills, this vol., p. 455), the constitution of which is represented by the general formula I (in which R indicates an alkyl radicle and X an acid radicle). The

may accordingly be regarded as *pseudocyanines* \* (II) in which the two quinoline nuclei are replaced by nuclei of benzothiazole.



In the present communication, a series of dyes is described which are intermediate between the thiocyanines and the *isocyanines* (III), in that they contain one quinoline and one benzothiazole nucleus. They are prepared by the action of sodium



hydroxide in alcoholic solution on a mixture of a quinoline alkylidide and a 1-methylbenzothiazole alkylidide. The method of their preparation thus corresponds exactly with that of the *isocyanines*; their composition is, moreover, analogous, differing from that of the *isocyanines* only in containing an atom of sulphur in place of the group  $-C_2H_2-$ , and their optical, photosensitising, and general chemical characters also show close relationships to those of the *isocyanines*. We therefore regard their formation as being due to an interaction between the reactive 1-methyl group of the 1-methylbenzothiazole alkylidide and the quinolinium *pseudo*-base, in which the latter plays the same part as in the *isocyanine* condensation. We accordingly consider that in these dyes the 1-methylbenzothiazole residue is linked to the 4-position of the quinoline nucleus and that their constitution is to be represented by formula IV. The acid radicle is regarded as being attached, in view of the virtual tautomerism of the cyanine dyes (this vol., p. 1489), to what is presumably the more basic part of the molecule (compare Mills and Wishart, T., 1920, **117**, 579).

On account of their close correspondence with the *isocyanines*, the name *thioisocyanine* is proposed for the dyes of this series.

Although in the *isocyanine* condensation the quinaldinium salt can be replaced by a 1-methylbenzothiazole alkylidide, the converse replacement, namely, that of the quinolinium salt by a quaternary salt of benzothiazole, cannot be made. This appears to be due to the instability of the *pseudo*-bases derived from the benzothiazole alkylidides. It is, however, possible to bring about the

\* These dyes, discovered by O. Fischer and Scheibe (*J. pr. Chem.*, 1919, [ii], **100**, 86), were named by them *pseudoisocyanines*.



coupling of benzothiazole alkylidides with quinaldinium or lepidinium salts indirectly by a method which we hope shortly to describe. From lepidine ethiodide and benzothiazole ethiodide, a dye is thus produced which is identical with the thioisocyanine formed from quinoline ethiodide and 1-methylbenzothiazole ethiodide by the action of alcoholic sodium hydroxide. This fact, together with those described in the present communication, establishes the constitution of the thioisocyanines (except for the question of the position of the acid radicle).

It is interesting that Hofmann, who first obtained cyanine dyes from the benzothiazole bases (the carbothiocyanines; this vol., p. 455)—although he regarded them incorrectly as analogues of cyanine itself (*Ber.*, 1887, 20, 2264)—apparently also observed the production of the thioisocyanines in an impure condition. He states (*loc. cit.*, p. 2265) that experiments to "cross" the amyliodides of the quinoline bases with those of the benzothiazole bases (by heating them together in presence of aqueous ammonia) yielded dyes which gave extraordinarily intense deep red solutions in alcohol, but could not be obtained in crystalline form.

The thioisocyanine iodides are bright red compounds which crystallise exceedingly well from alcohol. Their orange-red alcoholic solutions show a pair of overlapping absorption bands of unequal intensity in the green and bluish-green; the crest of the deeper band lies in the neighbourhood of wave-length  $\lambda$  5000—5100, that of the less intense has a wave-length about  $\lambda$  120—150 shorter. In general appearance, the absorption spectra of the thioisocyanines are very similar to those of the isocyanines, but the bands in the former lie nearer to the blue end of the spectrum—the difference in wave-length being roughly  $\lambda$  500. This is in accordance with the fact, to which attention has recently been directed (this vol., p. 459), that benzothiazole derivatives are less deeply coloured than the corresponding quinoline compounds. The thioisocyanines are powerful photosensitisers for the green, giving an extra sensitisation to the gelatino-bromide plate extending to about  $\lambda$  5800. As with other cyanine dyes, their aqueous-alcoholic solutions are decolorised by the addition of mineral acids.

#### EXPERIMENTAL.

2:1'-Diethylthioisocyanine Iodide.—Quinoline ethiodide (7.2 grams) and 1-methylbenzothiazole ethiodide (7.7 grams) were dissolved in hot alcohol (100 c.c.), and a solution of sodium (0.69 gram) in rectified spirit (40 c.c.) was added. The solution, which immediately developed a deep red colour, was boiled for fifteen minutes and then allowed to cool. Bright red needles

separated (1—1.5 grams), which, after repeated recrystallisation from methyl alcohol, melted and decomposed at  $283^{\circ}$ . The crystals were dried at  $80^{\circ}/11$  mm. for analysis (Found: C = 54.60; H = 4.59; I = 27.75.  $C_{21}H_{21}N_2IS$  requires C = 54.78; H = 4.57; I = 27.61 per cent.).

The sensitisation spectrum shows a powerful band in the green extending, for moderate exposures, as far as about  $\lambda 5800$  with a maximum at  $\lambda 5250$ . There is an additional, very faint, band in the orange with a maximum at  $\lambda 6500$ . The absorption maxima lie at  $\lambda 5030$  and about  $\lambda 4890$ , respectively.

*5-Methyl-2:1'-diethylthioisocyanine iodide*, obtained by condensing together equimolecular quantities of quinoline ethiodide and 1:5-dimethylbenzothiazole ethiodide as above, crystallises from methyl alcohol in bright red needles which melt and decompose at  $269$ — $270^{\circ}$  (Found: I = 26.59.  $C_{22}H_{23}N_2IS$  requires I = 26.80 per cent.).

The sensitisation spectrum shows only the one band in the green extending, for moderate exposures, to about  $\lambda 5800$  with a crest at  $\lambda 5300$ . The two absorption bands have maxima at  $\lambda 5080$  and about  $\lambda 4920$ , respectively.

*1':6'-Dimethyl-2-ethylthioisocyanine Iodide*.—This dye, which was prepared from a mixture of *p*-toluquinoline methiodide and 1-methylbenzothiazole ethiodide, is less soluble than the two preceding. It crystallises from methyl alcohol in dark red, prismatic needles, m. p.  $306$ — $307^{\circ}$  (decomp.) (Found: I = 27.98.  $C_{21}H_{21}N_2IS$  requires I = 27.61 per cent.).

The sensitisation spectrum resembles that of the parent substance. The band in the green extends, for moderate exposures, to about  $\lambda 5750$ , the maximum lying at  $\lambda 5270$ . There is a second, weak band which has a maximum at  $\lambda 6450$  and is somewhat more pronounced than in the parent dye. The two absorption maxima lie at  $\lambda 5000$  and about  $\lambda 4870$ , respectively.

*5:1':6'-Trimethyl-2-ethylthioisocyanine Iodide*.—The dye, obtained from *p*-toluquinoline methiodide and 1:5-dimethylbenzothiazole ethiodide, crystallises from methyl alcohol in dark red needles, m. p.  $303^{\circ}$  (decomp.) (Found: I = 26.81.  $C_{22}H_{23}N_2IS$  requires I = 26.80 per cent.).

The extra-sensitisation comprises only the one band in the green, extending to about  $\lambda 5800$  with its maximum at  $\lambda 5310$ . The crests of the two absorption bands occur at  $\lambda 5070$  and about  $\lambda 4950$ , respectively.

*6-Ethoxy-2:1'-diethylthioisocyanine iodide* was prepared from a mixture of *p*-ethoxyquinoline ethiodide and 1-methylbenzothiazole ethiodide. The dye is obtained as bright red needles when its hot

saturated methyl-alcoholic solution is rapidly cooled, and as short, triclinic prisms terminated by domal planes by slow crystallisation from the same solvent. These crystals are deep red with a brassy lustre and appear to contain a molecule of solvent of crystallisation, which is given up when they are heated at  $80^{\circ}/12$  mm. (Loss in weight observed = 5.63.  $C_{23}H_{25}ON_2IS, CH_3 \cdot OH$  requires  $CH_3 \cdot OH = 5.97$  per cent.). Both modifications melt and decompose at  $262^{\circ}$  (Found :  $I = 25.45$ .  $C_{23}H_{25}ON_2IS$  requires  $I = 25.20$  per cent.).

The extra-sensitisation extends, for moderate exposures, to about  $\lambda 5750$  with a maximum at  $\lambda 5300$ ; there is also an extremely faint and indefinite continuation of the sensitisation into the orange, but no additional maximum is distinguishable. The two absorption bands have maxima at  $\lambda 5060$  and about  $\lambda 4930$ , respectively.

*6'-Ethoxy-5-methyl-2 : 1'-diethylthioisocyanine iodide*, obtained from *p*-ethoxyquinoline ethiodide and 1 : 5-dimethylbenzothiazole ethiodide, crystallises from methyl alcohol in bright red needles, m. p.  $269^{\circ}$  (decomp.) (Found :  $I = 24.80$ .  $C_{24}H_{27}ON_2IS$  requires  $I = 24.52$  per cent.).

The sensitisation spectrum shows only the one band in the green, extending to about  $\lambda 5800$ , with its maximum at  $\lambda 5350$ . The two absorption maxima lie at  $\lambda 5110$  and about  $\lambda 4990$ , respectively.

One of us (W. T. K. B.) is indebted to the Department of Scientific and Industrial Research for a grant for which he desires to express his thanks.

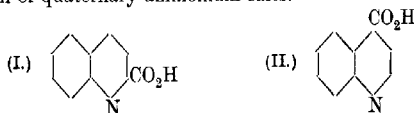
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## CCXLI.—The Quaternary Salts of Quinaldinic Acid.

By WILLIAM HOBSON MILLS and FRANCES MARY HAMER.

QUINALDINIC ACID (I) shows a striking difference from the isomeric cinchonic acid (II) in the resistance which it offers to the formation of quaternary ammonium salts.

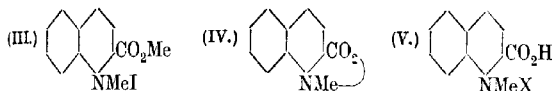


The latter acid, as was shown by Claus (*Annalen*, 1892, 270, 345), readily combines with methyl iodide to form a methiodide. Quinaldinic acid, however, we have found to be unattacked not

only by this reagent but even by the much more reactive methyl sulphate, which converts cinchonic acid under corresponding conditions into a quaternary salt of its methyl ester, thus esterifying the carboxyl group as well as combining with the tertiary nitrogen. It was also found by H. Meyer that the excellent method discovered by him for the conversion of pyridinecarboxylic acids into their betaines by digestion with an alkyl iodide and aqueous sodium carbonate fails completely with quinaldinic acid (*Monatsh.*, 1904, 25, 1196).

Quaternary salts of quinaldinic acid were accordingly unknown, but our attention was directed to them some time ago as possible oxidation products of the isocyanines and we prepared the methyl betaine and some of the methyl salts in order to become acquainted with their properties. When later we found that quinaldinic acid ethonitrate was the chief product of the oxidation of pinacyanol by nitric acid (T., 1920, 117, 1550), we also studied the preparation of the corresponding ethyl derivatives.

Although, as has been stated, quinaldinic acid itself could not be caused to combine with methyl sulphate, its methyl ester reacted readily with this substance at 100° giving a methyl-metho-sulphate, from which, by salting out with potassium iodide, methyl quinaldinate methiodide (III) was obtained.

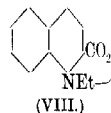
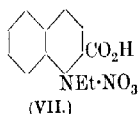
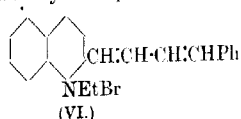


The contrast between the esters of quinaldinic and cinchonic acids with respect to the readiness with which they form quaternary salts is thus very much less marked than that between the acids themselves. This would indicate that the difference between the latter is only partly to be accounted for by steric hindrance; the carboxyl group probably has a greater effect in depressing the basic function of the nitrogen atom when in the 2-position than in the 4-position.

From methyl quinaldinate methiodide it was not found practicable to obtain quinaldinic acid methiodide by hydrolysing with dilute hydrochloric acid (though methyl cinchonate methiodide can be readily converted into the methiodide of the acid in this manner). The ester-methiodide was therefore treated in aqueous solution with silver oxide, for it seemed not improbable that when the ester grouping was thus brought into the molecule of a strong base intramolecular saponification would occur. Saponification did in fact take place under these conditions and quinaldinic acid methyl betaine was obtained in almost quantitative yield.

The pure betaine is a colourless, crystalline compound which melts at 142–145° and is exceedingly soluble in water, giving a neutral solution. From the methyl betaine various quaternary salts were prepared by addition of the corresponding acids.

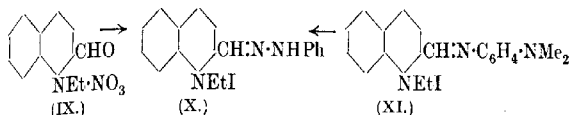
The analogous ethyl compounds proved much more difficult to obtain. We were unable to effect the addition either of ethyl iodide or of ethyl sulphate to methyl quinaldinate (or to 2-cyanoquinoline). We therefore attempted to prepare these compounds indirectly by oxidising a quinoline ethyl-salt with an unsaturated side-chain in the 2-position, hoping thus to discover a less costly source for them than pinacyanol. From benzylidenequinaldine ethonitrate or ethobromide we were unable to obtain a crystalline product. It appeared therefore that a substance with a still more oxidisable side-chain was required; we accordingly prepared cinnamylidenequinaldine ethobromide (VI) and from this, by



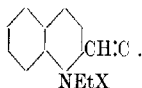
oxidation with nitric acid, we were able to obtain, with some difficulty, quinaldine acid ethonitrate (VII) identical with that obtained from pinacyanol (*loc. cit.*). From the nitrate the corresponding chloride was prepared and from this the betaine (VIII). These ethyl-salts, as well as the betaine, are exceedingly soluble in water. The betaine is rather unstable and shows a great tendency to decompose with the formation of dark-coloured products.

It is somewhat remarkable that the formation of quinaldine acid ethonitrate by oxidation with nitric acid should take place so much more smoothly from pinacyanol than from cinnamylidenequinaldine ethobromide. In connexion with the oxidation of derivatives of quaternary salts of quinoline which, like these, have an unsaturated side-chain attached in the 2-position, an observation of Besthorn and Giesselbrecht is of some interest. These authors found (*Ber.*, 1920, 53, [B], 1020) that the aldehyde-group in 2-aldehydequinoline-3-sulphonic acid is exceedingly resistant towards acid oxidising agents such as nitric acid or chromic acid. Apparently the ethonitrate of quinoline-2-aldehyde (IX) shows a similar behaviour, for we have been able to demonstrate its presence among the products obtained by somewhat prolonged treatment of pinacyanol with nitric acid. By extracting the crude oxidation product with acetone, a substance was obtained which gave with phenylhydrazine and subsequent treatment with potassium iodide a phenylhydrazone ethiodide (X) identical with that obtained by

Kaufmann and Vallette (*Ber.*, 1912, **45**, 1736) by the action of phenylhydrazine on the condensation product (XI) of nitroso-dimethylaniline and quinaldine ethiodide. The formation of the



aldehyde ethonitrate by oxidation in this manner is evidently a strong confirmation of the presence in pinacyanol of the grouping



#### EXPERIMENTAL.

##### A.—The Methyl Derivatives.

*Methyl Quinaldinate*.—This ester has been prepared by H. Meyer (*Monatsh.*, 1914, **25**, 1196) by the action of methyl alcohol on quinaldinoyl chloride. We found it could be very conveniently prepared by direct esterification of the acid. Concentrated sulphuric acid (18 c.c.) was added to a solution of quinaldnic acid (6 grams) in methyl alcohol (60 c.c.), and the mixture was boiled for two hours. On pouring the mixture into ice-cold water and neutralising with sodium carbonate, the ester separated and was then taken up in ether and dried. The residue left on evaporation of the ether solidified to a crystalline mass of the pure ester (Found : N = 7.7. Calc., N = 7.5 per cent.) of m. p. 86° (the melting point given by Meyer is 78°). The average yield was more than 80 per cent. of the theoretical.

*Methyl Quinaldinate Methiodide*.—Methyl quinaldinate (3 grams) was heated with methyl sulphate (2.4 grams, that is, a 10 per cent. excess of the theoretical quantity) for two hours at 100°. The yellow product, after having been digested with ether, was dissolved in a very little hot water and treated with powdered potassium iodide (6 grams). The methiodide thus precipitated, after recrystallisation from water, formed pale orange crystals, melting and decomposing at 122–129°. The yield of recrystallised product was 74 per cent. of the theoretical (Found : I = 38.43.  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{NI}$  requires I = 38.57 per cent.).

*Quinaldnic Acid Methyl Betaine*.—An aqueous solution of methyl quinaldinate methiodide (2 grams) was shaken with excess of freshly precipitated silver oxide, which was added a little at a time,

the mixture being finally warmed. A red solid separated at first but gradually disappeared. The solution was then filtered from the mixture of oxide and iodide of silver and evaporated to dryness in a vacuum over sulphuric acid, when the theoretical yield of betaine was obtained as an almost colourless, crystalline solid. After crystallising twice from absolute alcohol, from which solvent it separates in fairly large prisms, and carefully drying, it melted and decomposed between  $142^{\circ}$  and  $145^{\circ}$ , the exact temperature depending on the rate of heating (Found: C = 71.0; H = 5.2; N = 7.7.  $C_{11}H_9O_2N$  requires C = 70.6; H = 4.85; N = 7.5 per cent.). The betaine is exceedingly soluble in water or hot alcohol and slightly soluble in chloroform. From its alcoholic solutions, which readily become pink, it can be precipitated by ether in crystalline form.

*Quinaldinic Acid Methochloride.*—An aqueous solution of methyl quinaldinate methiodide (2 grams) was treated with silver oxide, and the filtrate, after acidification with hydrochloric acid, was evaporated to dryness. The residue was crystallised twice from absolute alcohol, in which it is moderately soluble. The salt was thus obtained as an almost colourless, crystalline compound melting and decomposing at  $158$ – $165^{\circ}$  (Found: C = 58.8; H = 4.8; N = 6.3; Cl = 15.7.  $C_{11}H_{10}O_2NCl$  requires C = 59.0; H = 4.5; N = 6.3; Cl = 15.85 per cent.). It is very soluble in water and, unlike the methyl betaine, is oxidised only very slowly in aqueous solution by potassium permanganate.

*Quinaldinic Acid Methonitrate.*—The aqueous solution of the betaine was acidified with nitric acid and evaporated to dryness. The salt thus formed was recrystallised twice from absolute alcohol. It was obtained in crystals melting and decomposing at  $138^{\circ}$  and very soluble in water (Found:  $NO_3$  = 24.9.  $C_{11}H_{10}O_2N \cdot NO_3$  requires  $NO_3$  = 24.8 per cent.).

#### B.—The Ethyl Derivatives.

*Cinnamylidenequinaldine Ethiodide.*—Cinnamylidenequinaldine has been described by Renz and Loew (*Ber.*, 1903, **36**, 4330), who prepared it by heating quinaldine and cinnamaldehyde with zinc chloride at  $150^{\circ}$  in a sealed tube. It can be more conveniently prepared by heating a mixture of quinaldine (13.2 grams), cinnamaldehyde (12 grams), and zinc chloride (3 grams) for ten hours at  $100^{\circ}$  and crystallising the product from alcohol.

We found some difficulty in obtaining the pure ethiodide by heating the base with ethyl iodide at  $100^{\circ}$ . The product always contained too low a percentage of iodine, and although by prolonged extraction with ether and further treatment with ethyl

iodide at  $100^{\circ}$  a product melting and decomposing at  $226-228^{\circ}$  and containing very nearly the correct percentage of iodine (Found:  $I = 31.1$ ,  $31.1$ .  $C_{21}H_{20}NI$  requires  $I = 30.7$  per cent.) could be obtained, it was simpler to prepare the iodide through the ethosulphate.

Cinnamylidenequinaldine (2 grams) was heated with ethyl sulphate (2.5 grams) for three-quarters of an hour at  $110-135^{\circ}$ . The resulting red solid, after washing with ether, was dissolved in hot aqueous alcohol, and a saturated aqueous solution of potassium iodide added. The ethiodide, which was precipitated, was digested with ether and recrystallised from alcohol (Found:  $I = 31.4$ . Calc.,  $I = 30.7$  per cent.).

*Cinnamylidenequinaldine Ethobromide.*—This was prepared similarly to the ethiodide, by the action of potassium bromide on the ethosulphate. It was thus obtained as red crystals, and after recrystallising from alcohol and drying, melted at  $213-214^{\circ}$  (Found:  $Br = 22.05$ .  $C_{21}H_{20}NBr$  requires  $Br = 21.82$  per cent.).

*Quinaldinic Acid Ethonitrate.*—This compound is most easily prepared by the oxidation of pinacyanol as we have described in a previous communication (*loc. cit.*). It can be obtained from cinnamylidenequinaldine ethobromide in the following manner. The ethobromide (5 grams) was added to dilute nitric acid (200 c.c.), obtained by mixing concentrated nitric acid ( $d$  1.42) with an equal volume of water. On warming, nitrous fumes were produced and an oil appeared which partly dissolved as the temperature rose. The mixture was then heated to boiling for two and a half hours, a current of steam being blown through without the volume of the liquid being allowed to increase. The solution, after cooling, was extracted with ether, and the aqueous layer evaporated. The residue was redissolved in water and, after extraction with chloroform, the aqueous layer was again evaporated. The rather sticky residue was digested with acetone, and the solid undissolved by the acetone was recrystallised twice from absolute alcohol. The colourless, crystalline compound (2.0 grams) thus obtained agreed in all its characters with the quinaldinic acid ethonitrate prepared from pinacyanol. It melted at  $108-109^{\circ}$ , and the mixture of the two preparations melted at the same temperature (Found:  $CO_2H = 17.0$ . Calc.,  $CO_2H = 17.0$  per cent.).

*Quinaldinic Acid Ethochloride.*—An aqueous solution of quinaldinic acid ethonitrate was evaporated with excess of concentrated hydrochloric acid which had been saturated with sulphur dioxide, the evaporation being conducted first on the water-bath, then in a vacuum at the ordinary temperature over sulphuric acid and soda-lime. The sulphuric acid formed by oxidation of the sulphur



dioxide was removed with barium chloride, and the dry residue obtained by evaporating the filtrate from the barium sulphate was extracted with hot absolute alcohol. The alcohol, on cooling, deposited the chloride in almost colourless crystals melting and decomposing at  $150^{\circ}$  with previous darkening. The salt is extremely soluble in water (Found: Cl = 14.77.  $C_{12}H_{12}O_2NCl$  requires Cl = 14.92 per cent.).

*Quinaldinic Acid Ethyl Betaine.*—An aqueous solution of quinaldinic acid ethochloride was shaken with excess of freshly precipitated silver oxide, added a little at a time, and the filtrate and washings were evaporated. The betaine was thus obtained in almost colourless crystals melting and decomposing at  $146$ – $148^{\circ}$  (Found: C = 71.5; H = 5.5; N = 6.9.  $C_{12}H_{11}O_2N$  requires C = 71.6; H = 5.5; N = 7.0 per cent.). The betaine is rather unstable and darkens on warming with alcohol, in which it is very soluble.

C.—*Formation of Quinaldinaldehyde Ethonitrate in the Oxidation of Pinacyanol.*

1:1'-Diethylcarbocyanine bromide (1 gram) was oxidised with nitric acid, and the resulting solution was treated in the manner which we have previously described (*loc. cit.*) for the preparation of quinaldinic acid ethonitrate. The quaternary ammonium salts formed in the oxidation were digested with acetone, which leaves the quinaldinic acid ethonitrate undissolved. The acetone solution thus obtained contains quinaldinaldehyde ethonitrate, as was shown in the following manner. The acetone was evaporated and the residue was dissolved in a little water and treated with an alcoholic solution of phenylhydrazine (0.24 gram). After two hours, a saturated aqueous solution of potassium iodide was added, when a red, crystalline compound (0.08 gram) was precipitated, which was identified as quinaldinaldehydephenylhydrazone ethiodide by comparison with a specimen of this compound prepared as described by Kaufmann and Vallette (*loc. cit.*) from the corresponding dimethylaminoanil.

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CAMBRIDGE.

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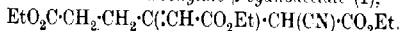
CCXLII.—*The Addition of Ethyl Sodiocynoacetate and Ethyl Sodiomalonnate to Ethyl Muconate.*

By ERNEST HAROLD FARMER.

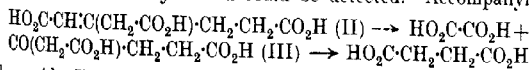
AMONG the very numerous exceptions to Thiele's theory of conjugation, the case of ethyl muconate,  $\text{EtO}_2\text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , is of considerable interest. Although the muconic system follows the rule in its 1:4-type of hydrogen addition, it has been shown recently by Chandrasena and Ingold (this vol., p. 1306) that ethyl muconate adds on bromine at the 1:2-position, a property which is unusual with symmetrical, conjugated chains. In view of this different behaviour of symmetrical addenda in relation to a symmetrical, conjugated system it seemed desirable to investigate the attachment of unsymmetrical addenda to ethyl muconate, and in this paper the addition of ethyl sodiocynoacetate and ethyl sodiomalonate is dealt with.

According to Hinrichsen (*Chem. Ztg.*, 1901, **316**, 43), addenda the components of which have an opposite polar character attach themselves at the 1:2-position. Ethyl muconate might therefore be expected to obey this rule were it not that even among the additive reactions of unsymmetrical, conjugated systems, on which alone Hinrichsen appears to have based his generalisation, there is at least one striking exception. Vorländer and his collaborators have shown (*Annalen*, 1906, **345**, 206) that although methyl cinnamylideneacetate, cinnamylideneacetone, and cinnamylideneacetophenone add on the components of ethyl malonate at the 1:2-position, methyl sorbate,  $\text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ , with the same substance yields a 1:4-additive product.

Remarkably enough, ethyl muconate follows neither of these courses, the product (90 per cent.) from ethyl sodiocynoacetate being *ethyl  $\Delta^2$ -butene- $\alpha\delta$ -dicarboxylate- $\beta$ -cyanonacetate* (I),



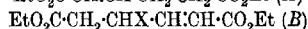
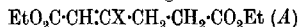
That the ester is correctly represented by this formula is seen from a study of its derivatives. By hydrolysis, a tricarboxylic acid (II) is obtained the constitution of which follows from its oxidation by alkaline potassium permanganate to a mixture of oxalic and succinic acids, probably by way of  $\beta$ -ketoadipic acid (III); no trace of tricarballic acid could be detected. Accompanying



the acid (II) is 2:6-dihydroxypyridine-4- $\beta$ -propionic acid (IV),  $\text{HO}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C} \begin{smallmatrix} \text{CH}\cdot\text{C}(\text{OH}) \\ \text{CH}\cdot\text{C}(\text{OH}) \end{smallmatrix} \text{N}$ , the production of which recalls

many similar occurrences during the hydrolysis of cyanoglutaconic esters and indicates that the parent ester is of the latter type.

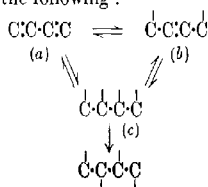
If, therefore, the addition be regarded as of the 1:2-type (B),



it is obvious that to yield the structure (A) the double bond must move from the  $\alpha$ - to the  $\alpha'$ -position, a phenomenon for which no parallel is to be found outside cyclic compounds. It is highly improbable that such a double movement occurs during addition, and that it is not brought about by hydrolysis is shown by the oxidation products of the ester (I) itself. The latter with alkaline potassium permanganate yields oxalic acid and ethyl hydrogen  $\alpha$ -cyano- $\beta$ -ketoadipate (V),  $\text{HO}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$  (Best and Thorpe, T., 1909, **95**, 1523), a derivative of the acid (III) assumed above to be an intermediate product of the oxidation of the tricarboxylic acid (II). It is necessary, therefore, to regard the addition as of the 1:3-type, such as has been observed in the case of normal ethyl  $\beta$ -methylglutaconate (Thorpe, T., 1919, **115**, 679), and of ethyl glutaconate (Ingold and Thorpe, T., 1921, **119**, 492).

Confirmation of this view regarding the additive process is gained from the similar action of ethyl sodiomalonate on ethyl muconate. In this case, the initial ester, *ethyl  $\Delta^2$ -butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate* (90 per cent.),  $\text{EtO}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C} \begin{smallmatrix} \nearrow \text{CH}\cdot\text{CO}_2\text{Et} \\ \searrow \text{CH}(\text{CO}_2\text{Et})_2 \end{smallmatrix}$  (VI), yields the foregoing tricarboxylic acid (II) on hydrolysis with mineral acids, whilst alcoholic sodium hydroxide produces a tetra-sodium salt corresponding with the above ester (VI), oxidisable to oxalic and succinic acids.

Thus it is clear that addition of ethyl cyanoacetate and ethyl malonate to ethyl muconate does not yield products with the components of the addendum in the 1:4-position after the manner of the addition of hydrogen to muconic acid or of bromine to butadiene, and only by sacrificing the directness of the facts can it be made to appear of a much modified 1:2-type. Therefore, to embrace all the phases of activity, views of the potentialities of the muconic four-carbon system must be extended and represented in some such way as the following:



Here the mobility of the system is represented as such that transformation from a state of ordinary unsaturation (*a*), with its 1 : 2-addition, to one of conjugation (*b*) with the associated 1 : 4-addition, can take place; further, under suitable conditions either may pass into a third state (*c*), where by the exercise of free valencies a 1 : 3-type of addition can occur.

A new investigation into the addition of esters to conjugated systems has been commenced with the hope of gaining further knowledge of the types of addition that occur and the circumstances of their manifestation.

#### EXPERIMENTAL.

*Ethyl Δ<sup>5</sup>-Butene-αδ-dicarboxylate-β-cyanoacetate* (I).—Sodium (2.3 grams) was "molecularised" under xylene and the latter replaced by absolute ether. To the cold mixture, ethyl cyanoacetate (13 grams) was added and the reaction allowed to proceed to completion. A dilute ethereal solution of well-dried ethyl muconate (20 grams) was then poured in, with shaking, and after the addition of a little absolute alcohol (30 c.c.) the containing flask was closed with a soda-lime tube and the whole kept at room temperature. The sodio-compound gradually dissolved to yield a clear reddish-brown liquid, and after one week this was shaken up with water, the ethereal layer separated, washed, and dried in the usual way, and the solvent evaporated, the residual yellow oil being almost pure *ethyl butenedicarboxylatemalonate* (yield 90 per cent.).

The ester distilled with some decomposition at 210°/20 mm. as a rather viscous, pale yellow oil, but at pressures above 20 mm. it decomposed almost entirely (Found: C = 57.81; H = 6.76.  $C_{13}H_{21}O_6N$  requires C = 57.88; H = 6.75 per cent.).

The alkaline aqueous layer yielded on acidification a small amount of a viscous, brown oil which gave an intense purple colour with ferric chloride. The amount was insufficient for a complete examination, but the substance appeared to consist essentially of an ethyl hydrogen ester of butenedicarboxylic-cyanoacetic acid admixed with a ketonic product of secondary condensation.

*Ethyl Δ<sup>5</sup>-Butene-αδ-dicarboxylate-β-malonate* (VI).—The preparation of this substance by the addition of ethyl sodiomalonate to ethyl muconate was effected in precisely the same way as the preceding one, except that no alcohol was added. *Ethyl butenedicarboxylatemalonate* was thus obtained as a pale yellow, fairly mobile oil. After removal of traces of ethyl malonate by steam distillation, an almost pure product was obtained (yield 90 per cent.). After distillation, which can be carried out at low pressures with only slight decomposition, it was obtained as a colourless

oil, b. p.  $215^{\circ}/14$  mm. (Found: C = 56.8; H = 7.2.  $C_{17}H_{22}O_8$  requires C = 57.0; H = 7.2 per cent.).

*Ethyl Hydrogen  $\Delta^{\alpha}$ -Butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate*.—The alkaline aqueous liquor yielded on acidification a small amount of red oil which gave an intense purple coloration with ferric chloride. On hydrolysis with concentrated hydrochloric acid, it yielded  $\Delta^{\alpha}$ -butene- $\alpha\delta$ -dicarboxylic- $\beta$ -acetic acid (II), and, after purification by reprecipitation from a solution of its sodium salt, gave figures which indicate that it is the triethyl hydrogen ester of butene-dicarboxylmalonic acid. The coloration with ferric chloride appears to be due to the presence of a trace of some ketonic condensation product (Found: C = 54.53; H = 6.30.  $C_{16}H_{22}O_8$  requires C = 55.54; H = 6.66 per cent.).

*2:6-Dihydroxypyridine-4-propionic Acid (IV)*.—Ethyl butene-dicarboxylatecyanoacetate (60 grams) was mixed with an equal volume of concentrated sulphuric acid and kept for five days. The hydrolysis was completed by adding water (120 c.c.) and boiling for twelve hours, removing the condenser at intervals to expel alcohol, but keeping the volume constant by addition of water. The sulphuric acid was removed by adding the boiling solution to the calculated quantity of barium hydroxide dissolved in 2 litres of boiling water. After rapid filtration by the aid of the pump, the clear filtrate deposited, on cooling, a considerable quantity of a solid crystallising in pale brownish-yellow flakes, which was recognised as a 2:6-dihydroxypyridine.

The liquor from which this substance separated was found still to contain a little sulphuric acid. It was therefore treated with small quantities of barium chloride solution until no more barium sulphate was precipitated. The filtered solution was evaporated to dryness several times with small quantities of hydrochloric acid. The residue having been extracted with acetone, the undissolved portion consisted mainly of the hydrochloride of the base. This was decomposed as accurately as possible with standard alkali, and the liberated base filtered off.

*2:6-Dihydroxypyridine-4-propionic acid* possesses marked acidic and basic properties. It acts as a dibasic acid, as might be expected of a substance with its constitution, and dissolves in mineral acids to produce salts. The *sulphate* and the *hydrochloride* are obtained as small, colourless needles on dissolving the compound in 50 per cent. sulphuric and concentrated hydrochloric acids respectively. Both these salts dissolve readily in cold water without appreciable dissociation.

*Dihydroxypyridinepropionic acid* is insoluble or only slightly soluble in the usual organic solvents, but in small amount can be

recrystallised from boiling water. Its solutions turn green or purple on standing, and the substance itself, on heating, darkens above  $250^{\circ}$  and decomposes at  $257^{\circ}$  [Found: C = 52.37; H = 4.96.  $C_8H_9O_4N$  requires C = 52.46; H = 4.91 per cent. 0.0862 neutralised 24.8 c.c. of 0.0385N-barium hydroxide. Calc. (dibasic), 24.5 c.c.].

*Ethyl  $\Delta^{\alpha}$ -Butene- $\alpha\delta$ -dicarboxylate- $\beta$ -acetate.*—The acetone extract (p. 2018) yielded on evaporation a brown syrup which would not solidify. It was therefore esterified with alcohol and sulphuric acid. The bulk of the ester distilled at  $195\text{--}205^{\circ}/19$  mm. as a colourless, mobile oil which gave, on hydrolysis with mineral acids, good yields of  $\Delta^{\alpha}$ -butene- $\alpha\delta$ -dicarboxylic- $\beta$ -acetic acid.

*$\Delta^{\alpha}$ -Butene- $\alpha\delta$ -dicarboxylic- $\beta$ -acetic Acid (Modification A) (II).*—This substance was obtained, not only from ethyl butenedicarboxylateacetate by hydrolysis with concentrated hydrochloric or dilute sulphuric acid, but also directly from ethyl  $\Delta^{\alpha}$ -butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate. The latter ester was boiled with concentrated hydrochloric acid until dissolution was complete, and, on cooling, a quantity of the acid separated out. A further quantity was obtained by concentrating the solution on a steam-bath. Extraction of the remaining liquor with ethyl acetate yielded a syrup from which another small amount of the solid acid was obtained by dissolving in dry ether and keeping for several days. The acid, which is only sparingly soluble in cold water and almost insoluble in dry ether, benzene, or chloroform, was recrystallised for analysis from ethyl acetate, from which it separated in colourless, crystalline aggregates melting at  $179^{\circ}$  without decomposition. Larger quantities were readily recrystallised by dissolving in hot water and adding an equal volume of concentrated hydrochloric acid. The unsaturated nature of the acid was shown by its instantaneous reduction of cold alkaline permanganate [Found: C = 47.62; H = 5.07.  $C_8H_{10}O_6$  requires C = 47.52; H = 4.95 per cent. 0.0608 neutralised 23.5 c.c. of 0.0385N-barium hydroxide. Calc. (tribasic), 23.5 c.c.]. The *silver* salt was obtained in the usual way as a white, curd-like precipitate (Found: Ag = 61.5.  $C_8H_7O_6Ag_3$  requires Ag = 61.9 per cent.).

Boiling acetyl chloride slowly converted the acid into its *anhydride*, the conversion being still incomplete after twenty hours. The anhydride was readily extracted from the mixture by boiling benzene, from which it separated in flattened needles melting at  $116^{\circ}$ . It dissolved in alkali with immediate hydration [Found: C = 52.4; H = 4.4; *M* (tribasic) = 184.  $C_8H_8O_5$  requires C = 52.2; H = 4.34 per cent.; *M* = 184]. Conversion into the original acid was brought about both by water and by concentrated potassium hydroxide.

The proportion of syrupy material increased when the process of hydrolysis was prolonged by using more dilute mineral acid. Analysis of the white, curd-like silver salt derived from the syrup gave figures inconsistent with a pure substance, but denoting a decrease of basicity.

*Sodium  $\Delta^{\alpha}$ -Butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate.*—Sodium (2.6 grams) was dissolved in absolute alcohol (45 c.c.) and to the cold solution water (5 c.c.) was added. On mixing with this solution ethyl  $\Delta^{\alpha}$ -butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate (10 grams) and heating for a short time on the steam-bath, a pale yellow, crystalline sodium salt was precipitated in almost quantitative yield. This was rapidly filtered and washed by repeated trituration with absolute alcohol. After drying in an evacuated desiccator, the pure salt was obtained as a pale yellow, very hygroscopic powder (Found: Na = 27.2.  $C_9H_8O_8Na_4$  requires Na = 27.5 per cent.).

*$\Delta^{\alpha}$ -Butene- $\alpha\delta$ -dicarboxylic- $\beta$ -acetic Acid (Modification B).*—Acidification of the deep yellow, aqueous solution of the tetra-sodium salt with the theoretical amount of dilute hydrochloric acid gave a colourless solution, from which, by repeated shaking with ether, an almost colourless gummy acid was extracted. This, on keeping in an evacuated desiccator, partly solidified, and the solid matter was separated by rubbing the mass with dry ether. The ethereal solution, on long keeping, deposited a further amount of the same substance, but the separation was by no means complete. A rather better result was obtained by repeating the process of desiccation and ether treatment until no further solid would separate.

The solid acid was extremely soluble in cold water, but almost insoluble in benzene or chloroform. It was recrystallised from ethyl acetate, from which it separated in colourless, crystalline aggregates of indefinite shape melting at  $152^{\circ}$ , but these crystals gave low results on analysis owing to retention of the solvent. The acid was therefore recrystallised by heating under reflux with a large volume of pure ether until it dissolved, crystallisation taking place on concentrating the solution. It was thus obtained as a white, crystalline powder still melting at  $152^{\circ}$ . After drying in the steam-oven, it gave the following figures: C = 47.2; H = 5.2 ( $C_9H_{10}O_8$  requires C = 47.5; H = 5.0 per cent.). 0.0632 neutralised 24.2 c.c. of 0.0385N-barium hydroxide. Calc. (tribasic), 24.3 c.c. The silver salt was obtained in the usual way as a white, curd-like precipitate (Found: Ag = 62.1.  $C_8H_7O_8Ag_3$  requires Ag = 61.9 per cent.).

That portion of the product of hydrolysis obtained in a solid condition represented only about 3 to 5 per cent. of the whole. The remainder, from which no further solid could be separated in any

way, was dissolved in boiling water and carefully neutralised with ammonia. Treatment of the cold solution with silver nitrate gave a white, curd-like silver salt, from which the acid was regenerated by decomposition with hydrogen sulphide in dry ethereal suspension. Evaporation of the solvent in a vacuum left the acid as a colourless, viscous gum, which on titration gave figures closely approximating to those required by the formula  $C_8H_{10}O_6$  (tribasic). It could not, however, be decided with certainty whether the substance was essentially an unsaturated acid or an isomeric lactonic acid. Complete analysis of the silver salt yielded figures scarcely more conclusive (Found: C = 18.02; H = 1.42; Ag = 60.0.  $C_8H_7O_6Ag_3$  requires C = 18.37; H = 1.34; Ag = 61.9 per cent.).

*Oxidation of (a)  $\Delta^8$ -Butene- $\alpha\delta$ -dicarboxylic- $\beta$ -acetic Acid, (b) Sodium  $\Delta^8$ -Butene- $\alpha\delta$ -dicarboxylate- $\beta$ -malonate.*—(a) To the less fusible acid (3 grams) in sodium hydrogen carbonate solution at 0°, 3 per cent. potassium permanganate was added drop by drop, with stirring. The equivalent of six atoms of oxygen was added before reduction ceased. The oxidation mixture, decolorised with sulphurous acid and freed from manganese oxide by steam treatment and filtration, was successively treated with dilute hydrochloric acid, ammonia, and calcium chloride. The precipitate thus obtained was found to consist entirely of calcium oxalate. Concentration of the alkaline mother-liquor to small bulk and subsequent acidification gave a liquid from which repeated extraction with ether removed a white, crystalline solid. This was contaminated with a minute amount of syrupy substance, but after washing with dry ether melted sharply at 185°, and proved to be succinic acid (mixed melting point). Careful examination of the residual liquor revealed no trace of tricarballic acid.

(b) The tetra-sodium salt (7 grams) was dissolved in water (300 c.c.) containing sodium hydrogen carbonate (3.5 grams) and the same procedure as above followed, except that the equivalent of only four atoms of oxygen was supplied. The results were identical with those of (a).

*Oxidation of Ethyl  $\Delta^8$ -Butene- $\alpha\delta$ -dicarboxylate- $\beta$ -cyanoacetate (I).*—The ester (14 grams), suspended in a solution of sodium hydroxide (14 grams) in water (500 c.c.) at 0°, was mechanically agitated while 3 per cent. potassium permanganate was run in. Reduction of the latter was rapid until the equivalent of three atoms of oxygen had been added, when it ceased. The cold, filtered reaction mixture was extracted many times with ether, and from the extract was obtained a considerable amount of a pale brown syrup which, after keeping for several weeks, partly solidified. Draining of the



semi-solid mass on a porous tile yielded a white solid, which, after recrystallisation from boiling water, was obtained as colourless needles melting at 104°. This substance gave in alcoholic solution a deep red colour with ferric chloride, titrated accurately as a dibasic acid, and agreed in all respects with ethyl hydrogen  $\alpha$ -cyano- $\beta$ -keto adipate (X) (Found: C = 50.69; H = 5.37. Calc., C = 50.68; H = 5.20 per cent.).

Oxalic acid could readily be obtained from the residues after boiling with alkali to complete the hydrolysis.

I desire to express my thanks to Professor J. F. Thorpe and Dr. C. K. Ingold for the interest they have taken in this research and to the Government Grant Committee of the Royal Society for a grant which has largely defrayed the cost of the materials employed.

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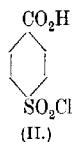
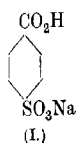
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### CCXLIII.—*p*-Dithiobenzoic Acid.

By SAMUEL SMILES and DOUGLAS CREESE HARRISON.

INVESTIGATION of *o*- and *m*-dithiobenzoic acids has shown that the reactions of the dithio-group in these substances are remarkably different and it thus became desirable to examine the behaviour of the para-isomeride. Although the ortho-derivative has been the subject of much investigation, *p*-dithiobenzoic acid has not yet been mentioned in literature, in fact, the only derivative of the type described seems to be the *p*-methylthiolbenzoic acid (IV) which was obtained by Zincke and Jörg (*Ber.*, 1910, **43**, 3448) from *p*-methylthiolaniline by replacement of the amino-group with carboxyl. In the preparation of *m*-dithiobenzoic acid (T., 1921, **119**, 1792), reduction of *m*-chlorosulphonylbenzoic acid proved to be the best method of obtaining the material in large quantity; a similar process has been found to be convenient for obtaining the desired para-compound. Technical *p*-toluenesulphonyl chloride serves as a convenient starting material; attempts were made to convert this substance directly to the desired *p*-chlorosulphonylbenzoic acid by oxidation with chromic anhydride in acetic acid solution, but the yields were poor and variable. The chloride was therefore converted to the sodium sulphonate, and this was oxidised in the usual manner, the resulting *p*-sulphobenzoic acid being isolated as the mono-sodium salt (I). The conversion

of this product to *p*-chlorosulphonylbenzoic acid (II) was readily accomplished by the action of hot chlorosulphonic acid. This method has obvious advantages over the usual method involving the use of phosphorus pentachloride: the partial hydrolysis of the dichloride is avoided, the crude product is sufficiently pure for immediate further treatment, and the yield is almost theoretical. Reduction of this chlorosulphonyl derivative gave good yields of the sulphinic acid (III) or of the corresponding thiol. Methylation of the latter gave the *p*-methylthiolbenzoic acid described by Zincke and Jörg (*loc. cit.*) and by Gattermann (*Annalen*, 1912, **393**, 226), whilst oxidation readily furnished *p*-dithiobenzoic acid. It has been previously recorded (T., 1921, **119**, 1795) that the dithio-group in *m*- and *o*-dithiobenzoic acids is resolved by the action of alkali hydroxide; preliminary experiments with the para-derivative indicate that a similar action takes place and that the reaction is much more rapid than in the case of the ortho-compound, which is undoubtedly the least reactive of the three isomerides.



#### EXPERIMENTAL.

*p*-Chlorosulphonylbenzoic Acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ .—The solution obtained by hydrolysis of 51 grams of *p*-toluenesulphonyl chloride with a slight excess of aqueous sodium hydroxide was nearly neutralised with dilute sulphuric acid and then mixed with 88 grams of potassium permanganate. Water was added to bring the volume of the solution to about 1½ litres, and this was heated until oxidation was complete. The oxides of manganese were removed and the colourless liquid was evaporated to about one-third of the original volume. After being mixed with excess of sulphuric acid, the solution was cooled, when the mono-sodium salt of *p*-sulphobenzoic acid separated. A further quantity of the product was obtained from the liquor by the addition of saturated brine, the total yield being 50 grams of crude material. A sample was purified by crystallisation, first from brine and then from hot water, in which it is freely soluble. Mono-sodium *p*-sulphobenzoate  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$ , after being dried in the air, contains 2 mols. of water of crystallisation, which are lost at 125–130° (Found:  $\text{H}_2\text{O} = 14.0$ ; Na, in anhydrous substance, = 10.2. Calc.,

$H_2O = 13.8$ ;  $Na = 10.27$  per cent.). This salt has been previously described as containing two and a half molecules (*Annalen*, 1875, 178, 279) and one molecule (*Ber.*, 1877, 10, 1715) of water of crystallisation.

Thirty-five grams of this anhydrous salt were heated with 50 c.c. of chlorosulphonic acid at  $100^\circ$  for about one hour, then the liquid was cooled and poured slowly over crushed ice. The colourless product was collected, washed with water, and dried; the yield was 30–35 grams. It may here be mentioned that in other experiments which are in progress it has been found that, in contrast with the meta- and para-compounds, *o*-chlorosulphonylbenzoic acid is very unstable and is readily decomposed by water in the neighbourhood of  $0^\circ$ . Hence it is evident that any of this ortho-compound which might have survived from the technical sulphonyl chloride used is at this stage eliminated. *p*-Chlorosulphonylbenzoic acid is moderately soluble in hot acetone, from which it separates in colourless needles; these melt and decompose at about  $235^\circ$ , the exact temperature depending on the rate of heating (Found:  $Cl = 15.87$ . Calc.,  $Cl = 16.09$  per cent. For complete interaction, 100 c.c. of *N*-NaOH required 7.43; calc., 7.35 grams).

*p*-Sulphinobenzoic Acid,  $CO_2H \cdot C_6H_4 \cdot SO_2H$ .—Twenty grams of *p*-chlorosulphonylbenzoic acid were suspended in 250 c.c. of water containing 70 grams of sodium sulphite. The mixture was shaken until all the chloride had dissolved, the liquid being kept weakly alkaline by repeated addition of small quantities of aqueous sodium hydroxide. When interaction was complete, excess of dilute sulphuric acid was added to the mixture, which was then kept for some hours to allow complete separation of the sulphinic acid. This was purified by crystallisation from hot water. *p*-Sulphinobenzoic acid forms colourless needles which are sparingly soluble in cold water and melt and decompose at about  $245^\circ$  according to the rate of heating (Found:  $S = 17.57$ .  $C_7H_6O_3S$  requires  $S = 17.2$  per cent. 100 c.c. of *N*-NaOH required 9.4; calc., 9.3 grams).

*p*-Thiolbenzoic Acid,  $CO_2H \cdot C_6H_4 \cdot SH$ .—Twenty grams of the carefully dried sulphonyl chloride were dissolved in about 75 c.c. of acetic acid. To the hot solution zinc dust and concentrated hydrochloric acid were added at intervals in small quantities. When reduction was nearly complete, the liquid became turbid, and ultimately a solid separated which increased in quantity after the liquid had been cooled and kept for a few hours. Hydrochloric acid was then added to remove excess of zinc, and the product was collected. About 11 grams of the dried thiol derivative were obtained. The product thus isolated formed a colourless, micro-

crystalline powder which decomposed at about  $250^{\circ}$  and was very sparingly soluble in all common solvents. The latter property combined with the liability of mercaptans to undergo oxidation renders the purification of the substance very difficult. For example, the substance is sparingly soluble in boiling nitrobenzene, but the crystalline material which separates from this solution was found by analysis to be a mixture of the disulphide with other oxidation products. Hence, for analysis, a sample of the substance was submitted to methylation with methyl sulphate in alkaline solution. The product after crystallisation from hot water melted at  $190^{\circ}$ ; Zincke and Jörg give  $192^{\circ}$  (*loc. cit.*), whilst Gattermann (*loc. cit.*) quotes  $190^{\circ}$  as the melting point of *p*-methylthiolbenzoic acid (Found: C = 56.9; H = 5.0; S = 19.5. Calc., C = 57.1; H = 4.8; S = 19.1 per cent.). The barium, silver, and copper salts of *p*-thiolbenzoic acid are sparingly soluble in water; they exist in two series, in one of which the carboxyl group alone is involved, whilst in the other both this and the thiol group take part. The salts of the latter type are the more soluble.

*p*-Dithiobenzoic Acid,  $[\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{S}]_2$ .—The dithio-acid is readily formed from the mercaptan by the usual methods of oxidation; it was most readily obtained by heating the latter substance in air at  $100^{\circ}$ . To prepare a pure sample of the dithio-acid the mercaptan was first purified by the following process. The crude material was dissolved in a slight excess of dilute ammonia, and the solution boiled until nearly neutral; the precipitate, which contained a small quantity of zinc, was removed and the mercaptan liberated by dilute hydrochloric acid. The product was again submitted to the same treatment and then boiled with water until all ammonium chloride was removed. At this stage oxidation to the disulphide was extensive, but the change was completed by heating the substance at  $100^{\circ}$  for some hours (Found: S = 21.1; C = 54.7; H = 3.6.  $\text{C}_{14}\text{H}_{10}\text{O}_4\text{S}_2$  requires S = 20.9; C = 54.9; H = 3.2 per cent.). *p*-Dithiobenzoic acid, prepared in this manner, formed a colourless powder which melted and decomposed somewhat above  $320^{\circ}$  and was insoluble in water and very slightly soluble in organic media. The following data illustrate the action of alkali hydroxide with the substance. A sample was dissolved in excess of cold *N*/2-sodium hydroxide; the free alkali was then estimated after the lapse of ten minutes and it was found that one molecular proportion of the disulphide had combined with 2.2 equivalents of sodium hydroxide. Under these conditions, the dithio-group evidently remains intact. A similar operation with a larger excess of alkali at  $100^{\circ}$  showed that decomposition was extensive, since 3.97 equivalents of alkali had combined with one

molecular proportion of the disulphide. Further experiments are required to show the exact relative stability of the three isomeric dithiobenzoic acids.

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CCXLIV.—*Reactions of Cellulose with Sodium Chloride and other Neutral Salt Solutions. Part I. Preliminary Survey.*

By HELEN MASTERS.

IN some experiments carried out by the British Scientific Instrument Research Association in connexion with tissue papers used for wrapping lenses, it was observed that some of the papers gave a slightly acid liquor on extracting with a solution of sodium chloride, although no acid could be detected in the aqueous extracts of these papers. Further observations indicated that the paper might possibly contain a trace of acid which could not be detected by the usual tests, but which was removed when the paper was extracted with the salt solution. As the chief problem under consideration, namely, that of providing a paper which would not produce tarnishing on a polished glass surface with which it was left in contact, had been satisfactorily solved, these investigations were not continued further, although the results were sufficient to indicate that a further study of the behaviour of cellulose with neutral salt solutions might prove of considerable interest.

In consultation with Sir Herbert Jackson it was agreed that such an investigation should be undertaken in conjunction with the British Scientific Instrument Research Association as an extra-mural research.

It is well known that some metallic substances are taken up by cellulose and that concentrated solutions of certain salts have a solvent action on it, but it appears to be generally accepted that cellulose is without action on dilute solutions of most neutral salts.

Schwalbe ("Die Chemie der Cellulose"), after summarising numerous observations which have been made on the reactions of cellulose with neutral salt solutions, expresses the opinion that there is no definite evidence that cellulose can decompose such solutions.

Harrison (*J. Soc. Dyers Col.*, 1912, **28**, 359), on the other hand, in studying the behaviour of cotton in relation to dyeing, observed

that when a solution of sodium chloride was filtered through purified cotton, hydrochloric acid passed through. The presence of this acid was detected by an electrolytic method, as the solution was too dilute for chemical analysis. The solution was found to have higher conductivity after than before filtration.

In the experiments made by the British Scientific Instrument Research Association, acid was extracted in sufficient quantity to react with neutral litmus and with methyl-orange.

In view of the difficulty of obtaining cellulose free from small traces of impurities, the liberation of acid from the cellulose on extraction with sodium chloride might be due, as already suggested, to the presence in the cellulose of a trace of acid which could not be washed out with water, but which was removed on extracting with sodium chloride. As, however, the existing evidence indicates that the quantity of acid liberated is likely to be extremely small and of such an order that it would not be detected by the ordinary methods of analysis, the liberation of the acid might also conceivably be due to some reaction between the cellulose and the salt solution. A reaction of this character would not necessarily be incompatible with the generally accepted view that sodium chloride is in the ordinary sense, where quantities of greater magnitude are involved, without action on cellulose.

In these investigations it was first of all necessary to obtain more definite evidence of the liberation of acid on the extraction of cellulose with sodium chloride, and in the event of acid being liberated to determine, if possible, whether this reaction was due to impurities in the cellulose or to some reaction between the cellulose and the salt solution.

The best quality cotton wool was selected as the most suitable material for these experiments, as this may be regarded as one of the purest forms of cellulose available in considerable quantity.

*Method.*—Freshly distilled water was used for washing the cotton and for preparing the required solutions. Its neutrality was tested immediately before use by titration with  $N/100$ -acid, using methyl-orange as indicator. The titrations were carried out in white porcelain dishes, and the amount of indicator added was carefully regulated. With good daylight illumination or with an inverted neandescent gas-lamp, a distinct colour change could be observed when 0.2 c.c. of  $N/100$ -acid was added to 100 c.c. of water, so that it should be possible by this method to detect the presence of 0.07 milligram of hydrochloric acid or its equivalent in 100 c.c. of water. Expressed in terms of hydrogen-ion concentration, this solution would give a value of  $P_H = 4$  to 5, and this is just within the limits of sensitiveness of the indicator.

The cotton was washed with water until at least two successive washings gave the same reaction as the water. In the first experiments, the cotton was steeped for about twenty-four hours, or in some cases boiled for one hour in the water, and the water decanted and tested. This method of washing was found to be extremely slow, and in the later experiments the cotton was packed tightly in a cylindrical glass funnel connected with a filter flask and pump. The stem of the funnel dipped into the water used for washing, and the water was drawn through the cotton and collected in the filter flask. In all these later experiments, the cotton, after washing with cold water until a neutral extract was obtained, was washed three or four times with boiling water and then again with cold water to ensure the removal, as far as possible, of soluble substances present in the cotton.

A neutral solution of sodium chloride was next passed through the washed cotton, the solution being tested both before and after passing through the cotton in the same manner as the water. The solution of sodium chloride which had passed through the cotton was found in all cases to be acid to methyl-orange, although several different samples of cotton were tried, some of which gave at first a slightly alkaline extract during the preliminary washing and others a slightly acid extract. The acidity of the solution which had passed through the cotton was determined by titration with  $N/100$ -alkali, using, as in the case of the water, 100 c.c. for each titration. If the extraction with sodium chloride was repeated several times, the amount of acid extracted rapidly decreased and after two or three extractions the extract became neutral.

If the liberation of acid is due to the salting out of some impurity in the cotton, it might be anticipated that extracting with sodium chloride until a neutral extract was obtained would remove this impurity and that the cotton thus treated and the original cotton might behave differently.

To test this point, the cotton which had been extracted with sodium chloride until a neutral extract had been obtained was next washed with water until the washings were free from chloride and neutral. On passing sodium chloride through this cotton, an acid extract was again obtained.

The processes of alternately extracting with water and with sodium chloride solution, in each case until a neutral extract was obtained, were repeated several times and acid was always extracted when the sodium chloride solution was passed through the washed cotton.

The amount of acid extracted in the successive experiments with sodium chloride was estimated in each case by titrating, with  $N/100$ -alkali, all the sodium chloride extracts which gave an acid

reaction and taking the sum of these titrations as equivalent to the total yield of acid for that experiment.

The acidity at first showed a tendency to increase, the amount of acid yielded in the second experiment being greater than obtained in the first, but afterwards the acidity appeared to approach a constant value and no evidence was obtained, as the experiments proceeded, of any decrease in the amount of acid extracted. It was also observed that when the cotton which had been treated with sodium chloride was subsequently washed with water the first washings had a slightly alkaline reaction. This alkalinity was very slight and decreased as the washing proceeded, but persisted through a number of washings, and some difficulty was experienced in completely freeing the cotton from alkali.

TABLE I.  
Ten grams of cotton. *N*/10-Sodium chloride.

Treatment.	Acid.		Alkali.	
	C.c. of <i>N</i> /100-acid.	Amount expressed in mg. of HCl.	C.c. of <i>N</i> /100-alkali.	Equivalent in mg. of HCl.
Preliminary washing .....	1.0	0.36		
I. <i>N</i> /10-Sodium chloride .....	6.0	2.2	12.0	4.4
Water .....				
II. <i>N</i> /10-Sodium chloride .....	10.8	3.9	11.2	4.1
Water .....				
III. <i>N</i> /10-Sodium chloride .....	10.4	3.8	11.2	4.1
Water .....				
IV. <i>N</i> /10-Sodium chloride .....	10.8	3.9	10.8	3.9
Water .....				
Average of II, III, and IV .....	10.7	3.9	11.1	4.0

The total alkali thus extracted was estimated from the sum of the titrations of all washings giving an alkaline reaction, and it was found that this alkali was, in most cases, approximately equivalent to the acid extracted from the cotton by the sodium chloride solution. As the extraction of this alkali extended over a considerable number of washings and the individual titrations were extremely small, very exact agreement could scarcely be expected.

Table I shows the results obtained in a typical experiment in which 10 grams of cotton were alternately extracted with water and with *N*/10-sodium chloride in each case until a neutral extract was obtained; 200 c.c. of liquid were used for each extraction. The acidity is expressed as milligrams of hydrochloric acid, and for



comparison the alkalinity is also expressed in this form. The acid extracted in the preliminary washing is included in this case in order to show that the amount is small compared with that subsequently extracted by the sodium chloride.

*Results with Sodium Chloride.*—The figures in Table I record the total amounts of acid and of alkali extracted in the successive experiments, but provide no comparison of the rates at which the acid and alkali were extracted from the cotton. For this reason, the results have also been expressed in a graphical form by plotting the volume of  $N/100$ -acid or alkali used for the titration of each extract.

FIG. 1.

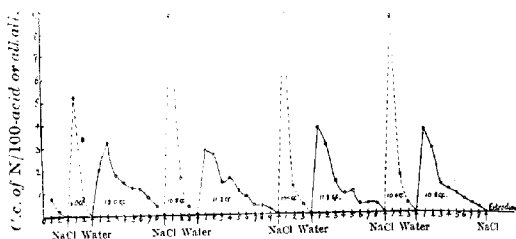
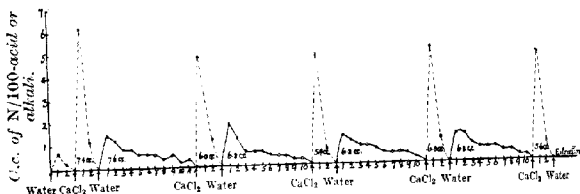


FIG. 2.



Thus, in Fig. 1, the dotted line represents the extraction of acid and the continuous line the extraction of alkali. The ordinates represent the number of c.c. of  $N/100$ -acid or alkali used for the neutralisation of each extract; so the sum of the ordinates in each portion of the curve gives the total volume of  $N/100$ -acid or alkali extracted in that stage of the experiment, and these are the amounts recorded in Table I. It will be seen that the extraction of the acid is much more rapid than the extraction of the alkali, and that at first the acid is low and the alkali in excess of this acid, but that afterwards the amounts of acid and alkali tend to become equivalent. Similar results were obtained in the earlier experiments in which the cotton was washed and extracted by steeping, but the amounts of acid and alkali extracted were smaller.

From the evidence thus furnished it appears that the liberation of acid by the action of sodium chloride on cellulose cannot be attributed, at any rate entirely, to the washing or salting out of acid originally present in the cellulose.

It has already been noted that similar results were obtained with several different samples of cotton, although some of these samples gave an acid extract on washing with water and some an alkaline extract.

Various experiments were made, modifying the preliminary treatment of the cotton. The cotton was washed with acid and with alkali, and was also extracted with alcohol and ether, and then, after washing until a neutral extract was obtained, extracted with the salt solution. In all cases acid was liberated when the cotton was extracted with the salt solution, and alkali when the cotton was subsequently extracted with water.

An experiment was also made with cotton purified in the manner described by Cross and Bevan ["Cellulose," Cross and Bevan, Longmans, p. 2 (1910)] for the isolation of cellulose from plant products. This purified cotton gave results which were in all respects similar to, and agreed closely with, those obtained with the untreated cotton.

The same type of reaction was observed when best quality filter-paper and also when lustra-cellulose was used instead of cotton. When carefully purified asbestos was subjected to the same treatment, no liberation of acid or alkali was observed.

It is intended to continue some experiments which have been made with wool, the results of which appear to indicate that alkali is liberated when the wool is extracted with salt solution, and acid when it is subsequently washed with water, this reaction being the reverse of that observed in the case of cotton. With the view of obtaining further data on which an explanation of the reactions observed in the case of cellulose could be based, the effect of varying the concentration of the salt solution and also the weight of cotton extracted was next examined.

*Further Experiments with Sodium Chloride.*—The amount of acid extracted by a 20 per cent. solution (3.4 *N*) of sodium chloride, was, on the average, the same as that extracted by a *N*/10-solution (3.9 mg. of HCl) and, as before, the acid yielded in the first experiment with sodium chloride was low.

On washing with water, the alkali washed out very irregularly. The washings were at first alkaline, then showed a tendency to become neutral, afterwards becoming alkaline again. The total alkali extracted by the water was slightly in excess of the acid extracted by the salt solution and was equivalent on the average to 4.3 mg. of HCl.

In an experiment in which 30 grams of cotton were extracted with  $N/10$ -sodium chloride, the average amount of acid extracted was 10.5 mg. of HCl, and the average amount of alkali was equivalent to 11.2 mg. of HCl. These figures correspond with 3.5 and 3.7 mg. of HCl, respectively, when calculated on 10 grams of cotton; so that the amounts are only slightly below the averages obtained in the previous experiments.

In view of the difficulty of extracting small quantities of acid and alkali completely from a relatively large amount of cotton and of obtaining absolute accuracy in the titration of such dilute solutions, the agreement may be taken as close enough to indicate that the acid extracted from the cotton by the sodium chloride is proportional to the weight of cotton extracted.

Cotton was also extracted with  $N/100$ -sodium chloride; the acid in this case averaged 3.0 mg. of HCl, and the alkali extracted on washing was equivalent to this acid.

*Effect of Temperature.*—If the temperature of the sodium chloride solution was raised to boiling point and the solution then passed through the cotton, the amount of acid extracted did not increase and no evidence could be obtained that the use of boiling water facilitated the removal of alkali in the subsequent washing. In some cases, on the contrary, the alkali appeared to be removed rather less rapidly with boiling water than with cold water, but there was no appreciable difference in the total amounts extracted.

The highly absorbent properties of cellulose and the very small amounts of acid and alkali liberated render it extremely difficult to obtain direct experimental evidence of the exact nature of the changes involved in the observed reactions, but it appeared that progress in this direction was most likely to be made by investigating the behaviour of other salt solutions under similar conditions.

*Other Salt Solutions.*—Completed experiments have so far only been made with a few salts, but it is intended that the examination shall be extended to a number of other salts.

In these experiments, 10 grams of cotton were extracted with a  $N/10$ -solution of the salt, using 200 c.c. for each extraction.

Ammonium chloride and sodium sulphate gave results in all respects similar to those obtained with sodium chloride, except that in the case of ammonium chloride the alkali washed out rather more readily. The amount of acid extracted with barium chloride and also with calcium chloride was considerably less than that extracted by sodium chloride, the average amount in both cases being 2.3 mg. of HCl. As indicated in Fig. 2, the washing out of the alkali was extremely slow, but the total alkali liberated was equivalent to the acid extracted by the salt solution.

With both these salts, the amount of acid extracted in the first experiment was slightly greater than that extracted in the succeeding experiments instead of less, as in the case of sodium chloride.

With cadmium iodide, which was chosen on account of its being only very slightly dissociated in water, the washings did not become alkaline; the cotton was washed twelve times with cold water, three times with boiling water, and then again with cold water between each treatment with the salt solution. The amount of acid extracted in the first experiment was greater than in the succeeding experiments, and the average amount of acid extracted was 1.2 mg. of HCl, which was less than that obtained with any other salt solution so far examined.

Acid was also liberated when a solution of sodium formate (slightly alkaline to litmus) was passed through washed cotton. The extract was neutral to methyl-orange but acid to litmus.

It has been noted that the amount of acid liberated on first extracting the cellulose with the salt solution is in all cases somewhat abnormal when compared with the amount of acid set free in the succeeding experiments when the acid liberated has reached a constant value, and it seems probable that the liberation of acid in the first experiment is influenced by certain factors which are not operative in the later experiments.

The amount of acid liberated by any particular salt is also likely to be in some degree dependent on the solubility of the corresponding basic hydroxide or on the extent to which it is possible to remove the base from the cellulose by extraction with water, that is, if the base is only partly removed from the cellulose by washing with water, then the retention of this base will tend to reduce the amount of acid set free when the cellulose shall be subsequently extracted with the salt solution.

Any attempt to remove the base more completely by washing with acid solutions instead of water between the extractions with the salt solution is likely to give rise to further difficulties, since in this case the possible effect of the retention of small quantities of acid in the cotton would have to be taken into consideration.

Some experiments are, however, being made using two different salt solutions alternately, that is, the cellulose is first extracted with one solution and then, after thorough washing with water, with the other solution. It seems likely that results may be obtained by alternating suitable solutions in this manner, which will make a more definite statement on these points possible. The possibility of freeing the cotton more completely from electrolytes by forcing water through it by electro-osmosis has also been considered, and a

few preliminary experiments have been made. The results already recorded are, however, sufficient to indicate that the reactions observed in the case of sodium chloride are not to be attributed to any special property of this salt, but are rather to be regarded as of a more general character and typical of the behaviour of a number of other neutral salts.

Since reactions of this order which would in the ordinary way escape detection are likely to be of considerable importance, not only in relation to the properties and reactions of cellulose, but possibly also in relation to other problems of colloidal chemistry, it has been thought advisable to extend the scope of the inquiry with the view of dealing with the whole subject, at a later date, on a more comprehensive basis than is at present possible.

In addition to obtaining further data for a number of representative salt solutions, the question as to whether these reactions are to be regarded as a special function of cellulose and are dependent on its chemical composition and fibrous structure or whether similar reactions are exhibited by other colloids and more especially by other fibrous material requires careful consideration. Experiments on these lines are now in progress. All that has been at present attempted is to give some account of the nature of the investigation and to record some of the more important results so far established in the course of this work.

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LONDON, W. 8.

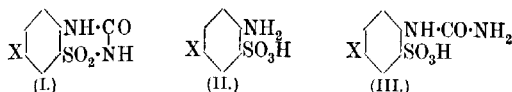
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# CCXLV.—*The Condensation of Aromatic o-Amino-sulphonic Acids with isoCyanic Acid.*

By JOHN RICHARD SCOTT and JULIUS BEREND COHEN.

It is well known that *o*-carbamidobenzoic acid and its substituted derivatives readily yield anhydrides (hydantoins) by the loss of a molecule of water; the object of the present research was to examine the possibility of obtaining compounds of a corresponding type (formula I) from *o*-carbamido-sulphonic acids. It has been found, however, that the latter do not form anhydrides so readily as the corresponding carboxylic acids, and it is still doubtful whether such an anhydride has been obtained. This agrees with the observation of Paal and Zitelmann (*Ber.*, 1903, **36**, 3343), who were unable to obtain the anhydride of  $\beta$ -phenylcarbamidoethane- $\alpha$ -

sulphonic acid, whereas Hoogewerff and van Dorp (*Rec. trav. chim.*, 1890, 9, 57) obtained that of  $\beta$ -phenylcarbamidopropionic acid.



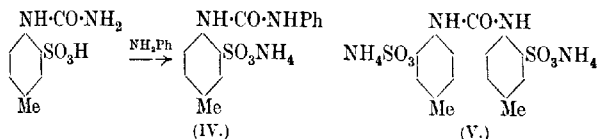
As no *o*-carbamido-sulphonic acid of the benzene series had been previously prepared, the action of isocyanic acid on a number of *p*-substituted aniline-*o*-sulphonic acids (II) has been investigated. The results may be summarised as follow :—

(1) When  $\text{X} = \text{NO}_2$ , isocyanic acid does not condense with the amino-group of the sulphonic acid.

(2) When  $\text{X} = \text{H}$ ,  $\text{CH}_3$ , or  $\text{SO}_3\text{H}$ , one molecule of isocyanic acid condenses with one molecule of the sulphonic acid, giving a carbamido-acid (III). Attempts were made to convert the latter into the anhydride (I) by the action of hydrochloric acid, acetyl chloride, or benzoyl chloride, but the acid was always recovered unchanged.

By the action of phosphoryl chloride on *p*-carbamidotoluene-*m*-sulphonic acid, a compound was obtained having the properties of an anhydride, but owing to the small amount obtained the analysis was unsatisfactory. The examination of this compound is being continued.

The action of aniline on *p*-carbamidotoluene-*m*-sulphonic acid has been found to take a somewhat unexpected course. By heating the acid with one molecule of aniline, it was thought that ammonium *p*-phenylcarbamidotoluene-*m*-sulphonate (IV) would be produced.

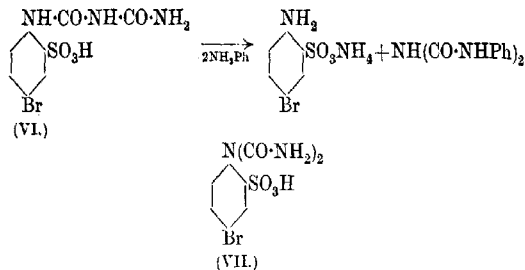


The products obtained, however, were *s*-diphenylcarbamide and ammonium *s*-di-*p*-tolylcarbamide-2 : 2'-disulphonate (V). When excess of aniline was used, *s*-diphenylcarbamide and *p*-toluidine-*m*-sulphonic acid were formed.

(3) When  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ , two molecules of isocyanic acid condense with one of the sulphonic acid, giving a derivative of *as*-phenylbiuret (VI); according to its mode of formation, the product might have either of the formulæ (VI) and (VII), but its constitution was proved by the following observations :—

(a) When *p*-bromophenylbiuret-*o*-sulphonic acid (VI) was heated

with excess of aniline at 160°, it was decomposed with the formation of *p*-bromoaniline-*o*-sulphonic acid and *s*-diphenylbiuret.



In the case of a compound having the constitution (VII), the action of aniline would probably result in the splitting off of the two carbamyl groups, which would be converted into *s*-diphenylcarbamide.

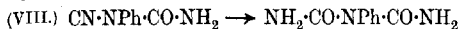
(b) According to Schiff (*Annalen*, 1907, **352**, 73), symmetrically substituted biurets ( $\text{NH}_2\cdot\text{CO}\cdot\text{NR}\cdot\text{CO}\cdot\text{NH}_2$ ) give the biuret reaction, whereas asymmetric derivatives ( $\text{NHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ) do not; our condensation products resemble the latter in giving no biuret reaction.

(c) Potassium *p*-bromophenylbiuret-*o*-sulphonate gives mono-acetyl and mono-benzoyl derivatives; a substance having formula (VII) would probably give di-substituted derivatives.

When these biuret derivatives are treated with nitrous acid, no nitrogen is liberated and the resulting solution gives only a pale yellow coloration on the addition of  $\beta$ -naphthol in sodium hydroxide solution. This affords a ready means of distinguishing these compounds from the carbamido-acids, which by the same treatment give nitrogen, and, with  $\beta$ -naphthol, an azo-colour. Incidentally, it was shown that *s*-disubstituted carbamides (for example, *s*-diphenylcarbamide and *s*-acetylphenylcarbamide) are also unaffected by nitrous acid.

As the failure of nitrous acid to react with the biuret derivatives was somewhat unexpected, it was decided to examine its action on the two phenylbiurets. *as*-Phenylbiuret was found to behave exactly like the products obtained by the action of isocyanic acid on the halogenoanilinesulphonic acids; but, unfortunately, we were unable to obtain the symmetrical compound. Schiff (*loc. cit.*) claims to have obtained *s*-phenylbiuret by the action of phosphorus trichloride on phenylcarbamide, but we were unable to isolate the compound. Büseken and Couvert (*Rev. trav. chim.*, 1910, [ii], **44**, 291) also failed to obtain it by this method. As it seemed probable

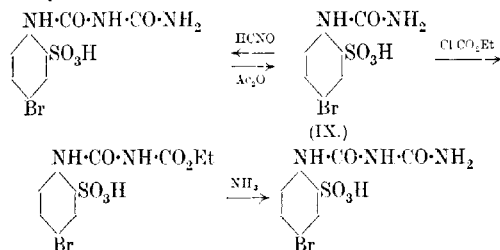
that *as*-phenyleyanocarbamide (VIII) would yield this substance by hydrolysis under suitable conditions,



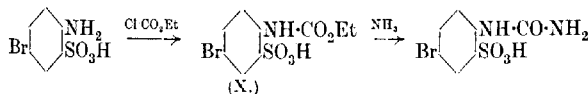
attempts were made to obtain the former compound, (*a*) by the condensation of phenyleyanamide with isocyanic acid, which proved unsuccessful, and (*b*) by the action of ammonia on phenyleyanurethane ( $\text{CN}\cdot\text{NPh}\cdot\text{CO}_2\text{Et}$ ). The urethane was readily obtained by the action of ethyl chloroformate on potassium phenyleyanamide ( $\text{NKPh}\cdot\text{CN}$ ), but the action of ammonia gave only a very small quantity of an impure product. The attempt to obtain *s*-phenylbiuret was therefore discontinued.

The exceptional behaviour of the *p*-halogeno-aniline-*o*-sulphonic acids in giving biuret derivatives by the action of isocyanic acid is not due to the influence of either the sulphonic acid group or the halogen atom alone, since, as we have shown, neither aniline-*o*-sulphonic acid nor *p*-bromoaniline yields biuret derivatives, and previous investigators have shown that *p*-chloro- and *p*-iodo-aniline give the corresponding carbamides.

In order to determine whether *p*-bromophenylcarbamide-*o*-sulphonic acid (IX) can be converted into the corresponding biuret compound by the action of isocyanic acid, or of ethyl chloroformate followed by ammonia,



the following methods for the preparation of the carbamido-acid are being investigated. (*a*) The sulphonation of *p*-bromophenylcarbamide; (*b*) the bromination of *o*-carbamidobenzenesulphonic acid; (*c*) the condensation of *p*-bromoaniline-*o*-sulphonic acid with ethyl chloroformate, and treatment of the resulting urethane (X) with ammonia.



The results of these experiments will be described in a later



communication, but it may be mentioned that the sulphonation of *p*-bromophenylcarbamide gives the desired product (IX), and *p*-tolylcarbamide may be converted in the same way into *p*-carb. amidotoluene-*m*-sulphonic acid, identical with the product here described (p. 2039); the potassium salt of (X) has also been obtained. *p*-Bromophenylcarbamide-*o*-sulphonic acid is also produced by the prolonged action of acetic anhydride on potassium *p*-bromophenylbiuret-*o*-sulphonate, and de-acetylation of the product.

The condensation of other *p*-substituted aniline-*o*-sulphonic acids with isocyanic acid is being investigated.

#### EXPERIMENTAL.

*p*-Nitroaniline-*o*-sulphonic Acid.—Equivalent amounts of sodium acetanilide-*o*-sulphonate (Claasz, *Annalen*, 1911, **380**, 309) and barium chloride were dissolved in the minimum quantity of boiling water. On cooling, barium acetanilide-*o*-sulphonate separated in small prisms. This was nitrated to give *p*-nitroaniline-*o*-sulphonic acid (Boyle, T., 1911, **99**, 329).

The potassium salt forms anhydrous, orange, rhombic plates, and is remarkable for its sparing solubility in water, being formed as a precipitate by the addition of a potassium salt to a solution of the acid. Even with a 0.1 per cent. solution of potassium chloride, a precipitate is formed after some time. The ammonium salt forms small, orange rhombohedra, sparingly soluble in cold water, and charring without melting at about 290°. The aniline salt separates from alcohol, in which it is not very soluble, in yellow, rhombic plates, decomposing without melting at 236–237°.

*Action of Potassium Cyanate on p*-Nitroaniline-*o*-sulphonic Acid.—

(a) On mixing aqueous solutions containing 1 mol. of the acid and 2 mols. of potassium cyanate respectively, an orange precipitate was thrown down. This, after recrystallisation from water, formed orange, rhombic plates and was proved to be potassium *p*-nitroaniline-*o*-sulphonate (Found: N = 11.21. Calc., N = 10.94 per cent.). The precipitation of this salt was almost quantitative.

(b) A solution containing 1 mol. of the nitro-acid, 1.5 mols. of potassium cyanate, and 0.5 mol. of hydrochloric acid in sufficient hot water to give a clear solution was evaporated to small bulk and cooled. Potassium *p*-nitroaniline-*o*-sulphonate again crystallised out almost quantitatively.

(c) One mol. of the nitro-acid, 2 mols. of the cyanate, and 4 mols. of hydrochloric acid were boiled for some time with a large volume of alcohol. The orange precipitate originally formed did not redissolve and was again shown to be potassium *p*-nitroaniline-*o*-sulphonate.

*p-Toluidine-m-sulphonic Acid*.—This acid, prepared according to von Pechmann (*Annalen*, 1874, **173**, 195), forms pale yellow needles which turn brown at 290° and above and decompose to a black mass at 312°. The *ammonium* salt consists of small, colourless prisms and melts with decomposition at 241–243°; the *aniline* salt crystallises from alcohol in needles melting with decomposition at 237–241°.

*Condensation with isoCyanic Acid*.—Twenty-five grams of *p*-toluidine-*m*-sulphonic acid (1 mol.) and 15.5 grams of potassium cyanate (1.5 mols.) were dissolved in 150 c.c. of water; the clear solution was treated with 6.4 c.c. of hydrochloric acid (0.5 mol.) and evaporated to dryness on the water-bath. The residue was dissolved in sufficient boiling water to make 130 c.c. of solution, which, after filtering, was kept over-night. The white, pasty mass which separated was filtered off and dissolved in a boiling mixture of 65 c.c. of hydrochloric acid and 65 c.c. of water. On cooling, *p*-carbamidotoluene-*m*-sulphonic acid crystallised out in small plates (15 grams). A little more, mixed with some *p*-toluidine-*m*-sulphonic acid, was obtained by concentrating the mother-liquors. The product was recrystallised from a mixture of three parts of water and two of hydrochloric acid.

*p*-Carbamidotoluene-*m*-sulphonic acid forms small, colourless, rectangular plates or prisms which become yellow at 210° and decompose at 222–223° (Found: in air-dried material, N = 11.60; H = 4.78, 4.71; H<sub>2</sub>O = 7.96; in material dried at 120°, C = 41.45; N = 12.01. C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>S.H<sub>2</sub>O requires N = 11.29; H = 4.85; H<sub>2</sub>O = 7.26. C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>N<sub>2</sub>S requires C = 41.74; N = 12.17 per cent.). It is very soluble in water, sparingly soluble in methyl or ethyl alcohol, and insoluble in other organic solvents. Owing to its sparing solubility in cold hydrochloric acid, it may be precipitated from an aqueous solution by the addition of hydrochloric acid, and is best crystallised from a mixture of the acid and water. On attempting to acetylate the acid by boiling it with excess of acetic anhydride, a clear solution was obtained, which, on standing, deposited crystals of *p*-toluidine-*m*-sulphonic acid (identified by its ammonium salt, prisms decomposing at 241°); no crystalline product could be obtained from the remaining liquid. It is therefore evident that boiling acetic anhydride breaks down the carbamido-group.

The *potassium* salt of *p*-carbamidotoluene-*m*-sulphonic acid crystallises from water, in which it is less soluble than the free acid, in small prisms which lose their water of crystallisation at 145° (Found: in air-dried material, K = 13.51; H<sub>2</sub>O = 5.98. C<sub>8</sub>H<sub>9</sub>O<sub>4</sub>N<sub>2</sub>SK.H<sub>2</sub>O requires K = 13.64; H<sub>2</sub>O = 6.29 per cent.).

The ammonium salt forms small, colourless prisms decomposing at  $258^{\circ}$  with effervescence. The aniline salt is prepared by heating the acid with aniline and alcohol. On cooling the clear solution, a mass of crystals separates; this, after recrystallisation from alcohol, in which it is very soluble, forms colourless needles or prisms, melting at  $170$ – $171^{\circ}$  to a liquid which soon resolidifies and then melts with decomposition at about  $247$ – $249^{\circ}$  (Found: N = 13.04.  $C_8H_{10}O_4N_2S_2C_6H_7N$  requires N = 13.00 per cent.).

*Potassium p-Acetylcarbamidotoluene-m-sulphonate.*—Potassium *p*-carbamidotoluene-*m*-sulphonate (4.5 grams) was boiled with 30 c.c. of acetic anhydride for one hour. After cooling, the solid was filtered off, washed with ether, dried in a vacuum, and twice recrystallised from boiling 70 per cent. alcohol. The fine, colourless needles thus obtained decomposed, with evolution of gas, at  $291$ – $293^{\circ}$  (Found: in air-dried material, K = 11.44;  $H_2O$  = 5.40; in material dried at  $115^{\circ}$ , C = 38.18; H = 3.43; N = 9.36.  $C_{10}H_{11}O_5N_2SK \cdot H_2O$  requires K = 11.89;  $H_2O$  = 5.49.  $C_{10}H_{11}O_5N_2SK$  requires C = 38.71; H = 3.55; N = 9.03 per cent.). Nitrous acid does not liberate nitrogen from this salt, and the resulting solution gives no azo-colour with alkaline  $\beta$ -naphthol; *p*-carbamidotoluene-*m*-sulphonic acid, under the same conditions, gives nitrogen and a deep red azo-colour. An attempt to obtain the free acid by treating the potassium salt with hydrochloric acid failed owing to the hydrolysis of the acetyl group.

By prolonged boiling of potassium *p*-carbamidotoluene-*m*-sulphonate with excess of acetic anhydride, a clear solution was formed, from which, by distilling off the acetic anhydride under reduced pressure and crystallising the residue from alcohol, small, colourless plates decomposing at  $261^{\circ}$  were obtained (Found: N = 4.94 per cent.). This was probably potassium *p*-acetylaminotoluene-*m*-sulphonate (Calc., N = 5.24 per cent.) or potassium *p*-diacetylaminotoluene-*m*-sulphonate (Calc., N = 4.53 per cent.).

*Action of Phosphoryl Chloride on p-Carbamidotoluene-m-sulphonic Acid.*—Eight grams of the acid were boiled with 35 c.c. of phosphoryl chloride for ten to fifteen minutes, when a clear solution was obtained. After distilling off most of the chloride, the residue was poured into 130 c.c. of water, and the mixture boiled for some time. The aqueous solution, on evaporation, yielded crystals of *p*-toluidine-*m*-sulphonic acid (yellow needles, decomposing at  $309^{\circ}$ ; ammonium salt, small prisms, m. p.  $242$ – $243^{\circ}$  with decomposition). The insoluble, sticky residue, when treated with hot acetone, partly dissolved, leaving a white powder, insoluble in water or alcohol and remaining unchanged below  $320^{\circ}$ . The acetone solution, on standing, deposited a white substance, which was twice extracted with boiling acetone.

On pouring the extracts into water, a crystalline precipitate was thrown down; this was redissolved in boiling acetone, and water added until crystals began to form. On cooling, colourless, thin, rhombic plates separated, which weighed 0.2 gram and decomposed at 272.5° (Found: in air-dried material,  $H_2O = 14.50$ ; in material dried at 120°,  $N = 11.75$ .  $C_8H_8O_3N_2S \cdot 2H_2O$  requires  $H_2O = 14.52$ .  $C_8H_8O_3N_2S$  requires  $N = 13.21$  per cent.). This compound contains nitrogen and sulphur, but neither chlorine nor phosphorus. It dissolves sparingly in water, giving a neutral solution, and is not acted on by sodium carbonate solution.

*Action of Aniline on p-Carbamidotoluene-m-sulphonic Acid.*—(a) 2.5 Grams of the acid (1 mol.) were ground with 0.95 gram of aniline (1 mol.) until they were converted into a solid mass of the aniline salt. This was heated to 170–175°, at which temperature it melted to a viscid liquid, which soon resolidified. After keeping at 175° for thirty minutes, the mass was cooled, boiled with 50 c.c. of water, and filtered. The insoluble residue (1.0 gram), after two recrystallisations from alcohol, formed colourless needles, m. p. 237.0–237.5°. It was identified as *s*-diphenylcarbamide by a mixed melting-point determination (m. p. of mixture, 236.5–237.0°) with an authentic specimen (m. p. 237.5°). The aqueous filtrate was evaporated to 10 c.c. and, on cooling, small pale yellow plates separated, which decomposed with vigorous effervescence at 275–276°. These were boiled with a little potassium hydroxide solution until no more ammonia was evolved; the clear solution, on cooling, deposited a quantity of minute, colourless plates, which were recrystallised from 60 per cent. alcohol, and dried over sulphuric acid. *Potassium s-di-p-tolylcarbamide-2 : 2'-disulphonate* was thus obtained as minute, anhydrous needles or plates (Found:  $N = 6.10$ ;  $K = 16.21$ .  $C_{15}H_{14}O_7N_2S_2K_2$  requires  $N = 5.88$ ;  $K = 16.38$  per cent.). This compound gives no azo-colour when treated with nitrous acid and alkaline  $\beta$ -naphthol. The yellow plates decomposing at 275–276° were evidently the corresponding ammonium salt.

(b) *p*-Carbamidotoluene-*m*-sulphonic acid was heated with an equal weight of aniline (3 mols.) at 160° for some time. The mixture, after first liquefying, gradually solidified to a pink mass, which, having been ground with ether to remove unchanged aniline, was boiled with dilute sodium carbonate solution. The insoluble residue, after recrystallisation from alcohol, melted at 236.5–237.0° and was identified as *s*-diphenylcarbamide. The aqueous solution, on evaporation, yielded pink, narrow plates, which evidently consisted of sodium *p*-toluidine-*m*-sulphonate, as on treatment with dilute hydrochloric acid *p*-toluidine-*m*-sulphonic acid was formed

(pale yellow needles, decomposing at  $311^{\circ}$ ; ammonium salt, prisms, decomposing at  $242^{\circ}$ ).

*Aniline-o-sulphonic Acid*.—*p*-Bromoaniline-*o*-sulphonic acid was debrominated by boiling with zinc dust and sodium hydroxide, as described by Kreis (*Annalen*, 1895, **286**, 385), but the process was continued for nine to ten hours (the six hours recommended by Kreis being insufficient) and the zinc was precipitated from the filtered liquid by saturating with carbon dioxide, instead of acidifying with hydrochloric acid and then precipitating with sodium carbonate.

The *aniline* salt forms colourless needles or prisms melting indefinitely at  $180$ — $210^{\circ}$  with decomposition.

*Condensation with isocyanic Acid*.—A mixture of 15 grams of the sulphonic acid (1 mol.), 10.5 grams of potassium cyanate (1.5 mols.), 4.3 c.c. of hydrochloric acid (0.5 mol.), and 100 c.c. of water was evaporated to dryness and the residue recrystallised from boiling water (sufficient to make 90 c.c. of solution) as described under the condensation of *p*-toluidine-*m*-sulphonic acid with *isocyanic* acid. The pasty mass which separated on standing over-night was filtered off, well pressed on a porous plate, and dried in a vacuum. The product (12 grams) was dissolved in 15 c.c. of boiling water, and 35 c.c. of hydrochloric acid were added. On cooling and scratching the sides of the containing vessel, *o*-carbamidobenzenesulphonic acid separated out in small plates (7 grams). It was recrystallised from a mixture of equal volumes of water and hydrochloric acid.

*o*-Carbamidobenzenesulphonic acid forms colourless, rhombic or hexagonal plates, decomposing at  $215$ — $230^{\circ}$  (Found: in air-dried material, N = 11.99;  $H_2O$  = 8.40.  $C_7H_5O_4N_2S \cdot H_2O$  requires N = 11.97;  $H_2O$  = 7.69 per cent.). In its properties it resembles *p*-carbamidotoluene-*m*-sulphonic acid, but is more soluble in water and in dilute hydrochloric acid than the latter compound.

The *potassium* salt forms colourless, hexagonal plates, much less soluble in water than the corresponding acid (Found: in air-dried material,  $H_2O$  = 7.00; in material dried at  $140^{\circ}$ , K = 15.31.  $C_7H_5O_4N_2SK \cdot H_2O$  requires  $H_2O$  = 6.62.  $C_7H_5O_4N_2SK$  requires K = 15.35 per cent.).

The *ammonium* salt, small, colourless prisms, melts with evolution of gas at  $237^{\circ}$ . The *aniline* salt (prepared like aniline *p*-carbamidotoluene-*m*-sulphonate) crystallises from a mixture of alcohol and chloroform in colourless needles, m. p.  $159$ — $161^{\circ}$  (with decomposition).

*Potassium o*-Acetylcarbamidobenzenesulphonate.—Potassium *o*-carbamidobenzenesulphonate was acetylated as described under potassium *p*-acetylcarbamidotoluene-*m*-sulphonate. The acetyl

derivative forms colourless needles which remain unchanged below  $310^{\circ}$  (Found: in air-dried material,  $K = 11.94, 11.97$ ;  $H_2O = 5.91$ .  $C_9H_9O_5N_2SK_2H_2O$  requires  $K = 12.42$ ;  $H_2O = 5.73$  per cent.). Its behaviour towards nitrous acid is the same as that of the corresponding toluene derivative.

*Aniline-2:4-disulphonic Acid.*—This was prepared by the sulphonation of sulphanilic acid (Zander, *Annalen*, 1879, **198**, 1), but the yield was very poor.

*Condensation with isoCyanic Acid.*—Two grams of the sulphonic acid (1 mol.) and 1.3 grams of potassium cyanate (2 mols.) were dissolved in a little water, and the mixture was evaporated to dryness on the water-bath. The residue was dissolved in a little boiling water, and hot alcohol added until a slight turbidity was produced, which was then redissolved by boiling. On cooling, the solution slowly deposited a flocculent mass of microscopic needles, which was recrystallised from alcohol and water in the same manner and finally dried over sulphuric acid.

*Potassium phenylcarbamide-2:4-disulphonate* was thus obtained as a white powder, very soluble in water but insoluble in alcohol (Found: in air-dried material,  $N = 7.55$ ;  $H_2O = 4.85$ ; in material dried at  $130^{\circ}$ ,  $K = 21.14$ .  $C_7H_6O_7N_2S_2K_2H_2O$  requires  $N = 7.18$ ;  $H_2O = 4.62$ .  $C_7H_6O_7N_2S_2K_2$  requires  $K = 20.97$  per cent.). This compound is decomposed by nitrous acid with liberation of nitrogen, and the addition of alkaline  $\beta$ -naphthol then produces a deep red azo-colour.

*Condensation of p-Bromoaniline with isoCyanic Acid.*—*p*-Bromoaniline (1 mol.) was dissolved in dilute hydrochloric acid (2.5 mols.) and treated with an aqueous solution of potassium cyanate (2.5 mols.). The pasty mass which soon separated was filtered off and recrystallised from alcohol. The product was identified as *p*-bromophenylcarbamide (Found:  $N = 13.20$ . Calc.,  $N = 13.02$  per cent.). It formed colourless needles, decomposing and charring without melting at  $265^{\circ}$  upwards; Richter (*Ber.*, 1891, **24**, 4172) describes *p*-bromophenylcarbamide as "decomposing at  $260^{\circ}$  without melting." Nitrous acid acted upon it with liberation of nitrogen and formation of a diazonium salt.

*p-Bromoaniline-o-sulphonic Acid.*—This was prepared by a modification of the method of Kreis (*Annalen*, 1895, **286**, 381). *p*-Bromoacetanilide (125 grams) was sulphonated with fuming sulphuric acid (63 grams) as described by Kreis. The hard mass thus obtained was ground up with water and filtered after standing for two hours. The solid was added to a hot solution of 50 grams of anhydrous sodium carbonate in two litres of water, which was then boiled with animal charcoal and filtered hot. The acid was precipitated from

the filtrate by the addition of 120 c.c. of hydrochloric acid; after cooling, it was filtered off, well washed with cold water, and dried in a vacuum desiccator. A little more was obtained by concentrating the filtrate. The yield was 78 per cent. of the theoretical. The acid thus obtained was practically white and was free from a sparingly soluble impurity (insoluble in sodium carbonate solution) which was always present when the crude sulphonation product was simply recrystallised from boiling water, as recommended by Kreis.

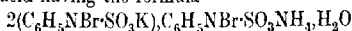
*p*-Bromoaniline-*o*-sulphonic acid crystallises in small plates (anhydrous) or needles (hydrated); both forms begin to darken at 270° and decompose to a black mass at 291°.

The *sodium* salt crystallises in small, pink, elongated plates, which are anhydrous (Found: Na = 8.40.  $C_6H_5O_3NBrSNa$  requires Na = 8.39 per cent.). The *ammonium* salt, small, colourless plates very soluble in water, melts at 226–227° to a liquid which rapidly acquires an intense purple colour.

The *aniline* salt was prepared by heating the acid with aniline and alcohol. The clear solution, on cooling, deposited colourless crystals, which were recrystallised from a mixture of alcohol and chloroform. *Aniline p-bromoaniline-o-sulphonate* forms small, glistening, colourless, rhombic plates, very soluble in alcohol and insoluble in chloroform (Found: N = 7.87, 7.82.  $C_6H_6O_3NBrS_2C_6H_7N$  requires N = 8.12 per cent.). It melts at 214° to a colourless liquid which soon becomes deep purple.

*Condensation with isoCyanic Acid*.—Seventy grams of the sulphonic acid (1 mol.) and 45 grams of potassium cyanate (2 mols.) were dissolved in 600 c.c. of cold water, and 27 c.c. of hydrochloric acid (1 mol.) added. The mixture was evaporated on the water-bath until it acquired a pasty consistency and was then dissolved in 600 c.c. of hot water. On cooling, a mass of small needles separated, which, after recrystallisation from hot water and drying over sulphuric acid, weighed 36 grams, and consisted of potassium *p*-bromophenylbiuret-*o*-sulphonate.

The mother-liquors from the crude product, on evaporation, yielded a quantity of pinkish-brown crusts. When these were dissolved in a little boiling water and the solution kept for some hours, a violet, pasty mass slowly separated. By repeating the recrystallisation three or four times, a pale violet, apparently amorphous powder was obtained, which approximated in composition to a double potassium ammonium salt of *p*-bromoaniline-*o*-sulphonic acid having the formula



(Found: C = 25.04; N = 6.54; S = 11.33; K = 9.77;  $H_2O$  = 2.40. Calc., C = 24.92; N = 6.46; S = 11.08; K = 9.01;

H<sub>2</sub>O = 2.08 per cent.). When this substance was heated alone or with sodium hydroxide solution, ammonia was liberated; and when treated with dilute hydrochloric acid, *p*-bromoaniline-*o*-sulphonic acid was formed (Found: in material dried at 130°, N = 5.00. Calc., N = 5.18 per cent.). The latter compound was further identified by preparing its aniline salt, small, rhombic plates which melted at 214–215°, and at 214° when mixed with an authentic specimen of aniline *p*-bromoaniline-*o*-sulphonate, in both cases forming a liquid which rapidly became purple. By careful crystallisation of the violet compound from water, a small quantity of pink plates, decomposing at 277–280°, was obtained; a similar substance, decomposing at 280°, was obtained by evaporating a solution containing the potassium and ammonium salts of *p*-bromoaniline-*o*-sulphonic acid. There is no doubt, therefore, that the violet compound is an impure double salt.

Potassium *p*-bromophenylbiuret-*o*-sulphonate forms small, colourless or faintly yellow needles, decomposing to a frothy mass at 210°. On attempting to estimate the water of crystallisation, the substance decomposed, but the analysis showed the salt to be dihydrated (Found: C = 23.39; H = 2.80; N = 10.28; S = 7.90; Br = 19.51; K = 9.53. C<sub>8</sub>H<sub>7</sub>O<sub>5</sub>N<sub>3</sub>BrSK.2H<sub>2</sub>O requires C = 23.30; H = 2.67; N = 10.19; S = 7.77; Br = 19.42; K = 9.47 per cent.). It is sparingly soluble in cold water, moderately soluble in hot water, and insoluble in alcohol. It dissolves readily in solutions of caustic alkalis to a reddish-violet solution. When treated with nitrous acid, no nitrogen is evolved and the resulting solution gives only a pale yellow coloration with alkaline β-naphthol; after standing over-night with the nitrous acid, β-naphthol produces a light red coloration (compare the action of nitrous acid on *as*-phenylbiuret, described below). Potassium *p*-bromophenylbiuret-*o*-sulphonate gives no biuret reaction, but is decomposed by sodium hypobromite with the liberation of two atoms of nitrogen (Found: N = 7.14. Calc., N = 6.80 per cent.). A hot aqueous solution of the salt, which has a yellow colour, is turned pink by the addition of dilute hydrochloric acid, and, on cooling, pink needles separate. These decompose at 181°, but consist of the unchanged salt (Found: N = 9.99 per cent.); on recrystallisation from water, the yellow colour is restored.

In some earlier experiments in which the *p*-bromoaniline-*o*-sulphonic acid was purified according to Kreis, instead of by the method described above, the product consisted of large, silky, yellow needles, decomposing at 181°. These, in spite of repeated crystallisation, gave unsatisfactory analyses (Found: K = 8.20, 8.41 per cent.); but by crystallisation from potassium hydroxide



solution and again from water, a pure product was obtained. This formed bright yellow needles, decomposing at  $181^{\circ}$ , in which the water of crystallisation could be estimated directly and which analysis showed to have the same composition as the substance decomposing at  $210^{\circ}$ , described above (Found: in air-dried material, N = 10.26; K = 9.55;  $H_2O$  = 8.73; in material dried at  $130^{\circ}$ , C = 25.53; H = 2.18.  $C_8H_7O_5N_3BrSK \cdot 2H_2O$  requires N = 10.19; K = 9.47;  $H_2O$  = 8.74.  $C_8H_7O_5N_3BrSK$  requires C = 25.53; H = 1.86 per cent.).

*p-Bromophenylbiuret-o-sulphonic Acid*.—Six grams of the potassium salt were added to a boiling mixture of 140 c.c. of hydrochloric acid and 60 c.c. of water. The salt dissolved and almost immediately the acid separated as a violet crystalline powder. After cooling, this was filtered off and dissolved in a little warm water; on adding hydrochloric acid, the sulphonic acid was reprecipitated and was then dried in a vacuum (Found: N = 12.43.  $C_8H_8O_5N_3BrS$  requires N = 12.27 per cent.). *p-Bromophenylbiuret-o-sulphonic acid* forms minute, pale violet plates or prisms, decomposing to a bulky froth at  $192^{\circ}$ . It is very soluble in water, moderately soluble in methyl or ethyl alcohol, and insoluble in other organic solvents and in hydrochloric acid. Its behaviour towards nitrous acid is the same as that of the potassium salt.

The *ammonium* salt, which is sparingly soluble in cold, and readily soluble in hot water, was obtained in two forms: colourless, hair-like needles, decomposing at  $194^{\circ}$ , and clusters of silky, bright yellow needles, decomposing at  $184^{\circ}$ . Both were formed simultaneously by the slow crystallisation of a solution of the salt; they are probably analogous to the two forms of the potassium salt described above.

The *aniline* salt, prepared by heating the acid with aniline and alcohol, separates from the clear solution thus obtained, in colourless, rhombic plates, which may be recrystallised from alcohol. It melts with decomposition at  $212^{\circ}$  (Found: Br = 18.73; S = 7.71.  $C_8H_8O_5N_3BrS \cdot C_6H_7N$  requires Br = 18.57; S = 7.42 per cent.).

*Potassium Acetyl-p-bromophenylbiuret-o-sulphonate*.—Three grams of potassium *p*-bromophenylbiuret-o-sulphonate were boiled with 30 c.c. of acetic anhydride for thirty minutes. The solid was filtered off, washed with ether, and recrystallised from hot water. The acetyl derivative was thus obtained as anhydrous, fine, colourless needles, sparingly soluble in cold water, and decomposing with evolution of gas at  $269$ – $270^{\circ}$  (Found: N = 9.84; K = 9.27.  $C_{10}H_9O_6N_3BrSK$  requires N = 10.05; K = 9.33 per cent.). When crystallised from 70 per cent. alcohol, it formed small, rhombic or hexagonal plates, decomposing at  $267^{\circ}$ , which were shown by the

iodoform reaction to contain alcohol of crystallisation (Found : loss on heating at  $140^{\circ} = 4.98$ .  $C_{10}H_9O_6N_3BrSK, \frac{1}{2}C_2H_6O$  requires  $C_2H_6O = 5.22$  per cent.).

By boiling potassium *p*-bromophenylbiuret-*o*-sulphonate with ten times its weight of acetic anhydride for one and a half hours, it was converted into a mass of flattened needles, which, after recrystallisation from hot water (with the addition of potassium carbonate to neutralise the acidity of the solution), formed colourless needles, remaining unchanged below  $310^{\circ}$ . This product gave no coloration with nitrous acid and alkaline  $\beta$ -naphthol, and was shown by analysis to be a somewhat impure specimen of *potassium acetyl-p-bromophenyl-carbamide-o-sulphonate* (Found : in air-dried material,  $H_2O = 4.77$ ; in material dried at  $125^{\circ}$ ,  $K = 9.94$ .  $C_9H_8O_5N_2BrSK, H_2O$  requires  $H_2O = 4.58$ .  $C_9H_8O_5N_2BrSK$  requires  $K = 10.40$  per cent.).

On dissolving this compound in boiling 70 per cent. hydrochloric acid and cooling, a substance separated, which, after recrystallisation from 50 per cent. hydrochloric acid, formed small, colourless, rhombic plates, decomposing to a dark, frothy mass at  $256-258^{\circ}$ , and reacting with nitrous acid with liberation of nitrogen and formation of a diazonium salt. It was identified as *p-bromophenylcarbamide-o-sulphonic acid* by analysis (Found : in air-dried material,  $H_2O = 8.01$ ; in material dried at  $130^{\circ}$ ,  $N = 9.67, 9.47$ .  $C_7H_7O_4N_2BrS, 1\frac{1}{2}H_2O$  requires  $H_2O = 8.38$ .  $C_7H_7O_4N_2BrS$  requires  $N = 9.49$  per cent.), and by comparison with an authentic specimen. The latter, obtained by the sulphonation of *p*-bromophenylcarbamide, consists of colourless, rhombic plates, containing  $1\frac{1}{2}H_2O$  and decomposing at  $256-260^{\circ}$ ; its *aniline* salt forms fine needles, m. p.  $183-184^{\circ}$ . The product obtained from potassium *p*-bromophenylbiuret-*o*-sulphonate gave an aniline salt, fine needles, m. p.  $183-185^{\circ}$ , and melting at  $182-184^{\circ}$  when mixed with an authentic specimen. This acid and its derivatives will be fully described in a later communication.

*Potassium Benzoyl-p-bromophenylbiuret-o-sulphonate*.—Potassium *p*-bromophenylbiuret-*o*-sulphonate (1 mol.) was dissolved in dilute potassium hydroxide solution (4 mols.) and shaken with benzoyl chloride (2 mols.). The mixture became warm and a mass of needles soon separated. This was filtered off, washed with alcohol and ether, and dried in a vacuum to remove benzoyl chloride, and recrystallised from water. The *benzoyl* derivative forms fine, colourless needles, decomposing at  $192-193^{\circ}$  (Found :  $K = 7.83$ ;  $H_2O = 8.80$ .  $C_{15}H_{11}O_6N_3BrSK, 2\frac{1}{2}H_2O$  requires  $K = 7.43$ ;  $H_2O = 8.59$  per cent.).

When a solution of potassium *p*-bromophenylbiuret-*o*-sulphonate (1 mol.) in aqueous potassium hydroxide (5 mols.) was shaken with

methyl sulphate (5 mols.), the latter soon disappeared and the clear solution slowly deposited minute plates, which, after recrystallisation from water, decomposed with evolution of gas at  $273^{\circ}$ . This was probably a methylated derivative of the original salt, but the amount obtained was insufficient for analysis.

*Action of Aniline on p-Bromophenylbiuret-o-sulphonic Acid.*—A mixture of 3 grams of the acid with 2.5 grams of aniline was heated at  $160^{\circ}$  until a clear liquid was obtained. After cooling, the solid mass was extracted with cold ether to remove excess of aniline, and then boiled with dilute sodium hydroxide solution. The insoluble residue was filtered off and recrystallised from alcohol. It then formed colourless needles or thin, rectangular plates, m. p.  $207-208^{\circ}$ , and was identified as *s*-diphenylbiuret by analysis (Found: N = 16.75. Calc., N = 16.47 per cent.) and by comparison with an authentic specimen. The latter crystallised from alcohol in needles or rectangular plates, m. p.  $208.0-208.5^{\circ}$ ; a mixture of the two specimens melted at  $207.0-207.5^{\circ}$ .

The alkaline aqueous solution, on evaporation, yielded pink plates, which proved to be sodium *p*-bromoaniline-o-sulphonate (Found: Na = 8.21. Calc., Na = 8.39 per cent.). This was further confirmed by converting it into the free acid, which gave an aniline salt, rhombic plates melting at  $212.5-214.0^{\circ}$  (to a purple liquid) and at  $212-213^{\circ}$  when mixed with an authentic specimen of aniline *p*-bromoaniline-o-sulphonate.

The condensation of *p*-bromoaniline-o-sulphonic acid with isocyanic acid, using only one molecule of the latter, gave the same biuret derivative, decomp.  $210-211^{\circ}$ , as when two molecules were used.

*p-Chloroaniline-o-sulphonic Acid.*—This was prepared by Paal's method (Ber., 1901, 34, 2753). The aniline salt (prepared like the corresponding bromo-compound) forms small, colourless, rhombic plates, melting at  $210^{\circ}$  to a brown liquid which soon resolidifies and decomposes on further heating. The condensation of this sulphonic acid with isocyanic acid was carried out exactly as for *p*-bromoaniline-o-sulphonic acid.

*Potassium p-chlorophenylbiuret-o-sulphonate* crystallises from water in fine, pink needles, which decompose with evolution of gas at  $185-190^{\circ}$  (Found: N = 11.80; K = 10.26;  $H_2O = 9.91, 9.94$ .  $C_8H_4O_5N_3ClSK \cdot 2H_2O$  requires N = 11.44; K = 10.63;  $H_2O = 9.81$  per cent.). With nitrous acid, no nitrogen is liberated, and on adding alkaline  $\beta$ -naphthol only a light yellow colour is produced.

*p-Chlorophenylbiuret-o-sulphonic Acid.*—This acid, prepared like the bromo-compound, forms minute, pink prisms, decomposing at  $181-182^{\circ}$ .

*p-Iodoaniline-o-sulphonic Acid*.—This was obtained by Boyle's method (T., 1909, 95, 1699). Its ammonium salt forms small, colourless plates which begin to darken at 220° and melt to a purple liquid at 224–226°. The aniline salt crystallises from alcohol in colourless, rhombic plates, m. p. 191.5°, to an intense purple liquid.

*Condensation with isoCyanic Acid*.—Ten grams of the sulphonic acid (1 mol.) were dissolved in a solution of 5.5 grams of potassium cyanate (2 mols.) in 125 c.c. of water; on adding 3.3 c.c. of hydrochloric acid (1 mol.) to the clear solution, a violet precipitate was produced. The mixture was then gently warmed on the water-bath until the precipitate was just redissolved, and immediately cooled. On scratching the sides of the containing vessel, potassium *p*-iodophenylbiuret-*o*-sulphonate gradually separated in flocculent masses of fine, violet needles; it was recrystallised from hot water. Care must be taken in this preparation not to heat the reaction mixture more than is necessary to dissolve the precipitate, otherwise no crystals will separate on cooling, and no crystalline product can be obtained by evaporating the solution to dryness. The yield is about 2.5 grams.

Potassium *p*-iodophenylbiuret-*o*-sulphonate forms minute, pale violet needles, sparingly soluble in cold, and moderately soluble in hot water; it sinters at 228° and decomposes with evolution of gas at 230–232°. It apparently crystallises with 1H<sub>2</sub>O, although the values obtained were rather high (Found: N = 9.84; H<sub>2</sub>O = 4.83; 4.68. C<sub>8</sub>H<sub>6</sub>O<sub>5</sub>N<sub>3</sub>ISK<sub>2</sub>H<sub>2</sub>O requires N = 9.52; H<sub>2</sub>O = 4.08 per cent.).

*p-Iodophenylbiuret-o-sulphonic Acid*.—This was prepared like the corresponding bromo-compound, using 1.5 grams of the potassium salt and 20 c.c. of 70 per cent. hydrochloric acid. It forms minute, grey prisms, decomposing at 198° to a bulky mass which then gradually melts (Found: N = 10.85. C<sub>8</sub>H<sub>6</sub>O<sub>5</sub>N<sub>3</sub>IS requires N = 10.91 per cent.). This acid and its potassium salt give only light yellow colorations with nitrous acid and alkaline β-naphthol.

The aniline salt crystallises from alcohol in small, diamond-shaped plates, m. p. 212–213°, with decomposition.

*Attempt to Condense Phenyleyanamide with isoCyanic Acid*.—Phenyleyanamide was obtained by Hofmann's method (Ber., 1885, 18, 3220) as colourless, flaky crystals, m. p. 35.5–36.5°.

(a) Phenyleyanamide did not dissolve on heating with an aqueous solution of potassium cyanate; on adding hot alcohol, a clear solution was obtained, from which a slight precipitate soon separated. The latter, after recrystallisation from alcohol, formed colourless needles, m. p. 181–183°, and was almost certainly triphenylisomelamine (the polymeride of phenyleyanamide), which forms

needles, m. p. 183°. The filtered solution, on cooling, deposited phenylecyanamide as an oil.

(b) A 90 per cent. alcoholic solution of equivalent amounts of phenylecyanamide and potassium cyanate was evaporated to dryness and the residue extracted with alcohol. After removing the insoluble matter (potassium carbonate), the solution was concentrated and allowed to crystallise. Potassium phenylecyanamide separated and was identified by conversion into phenylecyanamide (m. p. 35.0—36.5°). The latter was recovered almost quantitatively.

(c) Equivalent quantities of phenylecyanamide, potassium cyanate, and hydrochloric acid were dissolved together in alcohol. After standing over-night, the mixture was warmed on the water-bath for thirty minutes, and the potassium chloride filtered off. On adding water to the filtrate, phenylecyanamide separated as an oil which soon solidified and then melted at 36.0—36.5°.

*Phenylecyanourethane*.—8.2 Grams of ethyl chloroformate (14 mols.) were added to a solution of 8.7 grams (1 mol.) of potassium phenylecyanamide (Hantzsch and Osswald, *Ber.*, 1899, **32**, 650) in 100 c.c. of absolute alcohol at 25°; heat was evolved and potassium chloride precipitated. After warming on the water-bath for thirty minutes, the solution was filtered, the alcohol distilled off, and the residue dried in a vacuum. The resulting viscous oil was dissolved in 100 c.c. of ether, when some unchanged potassium phenylecyanamide separated. The filtered ethereal solution was dried with anhydrous sodium sulphate, and the ether distilled off. The viscous residue, on drying in a vacuum, solidified to a hard waxy mass (8.6 grams) of crude phenylecyanourethane, m. p. 30—31°. It was purified by dissolving in a little acetone, pouring into a large volume of water, and shaking until the precipitated oil solidified; after filtering off, it was dried in a vacuum.

*Phenylecyanourethane* is a colourless, waxy solid, m. p. 35.0—35.5°, b. p. 160—162°/16 mm. (with some decomposition) (Found: N = 14.81.  $C_{10}H_{10}O_2N_2$  requires N = 14.74 per cent.). It is extremely soluble in alcohol, acetone, or ether, readily soluble in benzene, insoluble in cold, but soluble in hot, light petroleum, and insoluble in water. Attempts were made to crystallise it by cooling solutions in benzene, light petroleum, alcohol-water, or acetone-water in a freezing mixture, but the substance always separated as an oil, which slowly solidified.

*Action of Ammonia on Phenylecyanourethane*.—Eight grams of the urethane were heated in a sealed tube for five hours at 110° with 70 c.c. of saturated alcoholic ammonia. After distilling off the alcohol, and drying the residue in a vacuum, the resulting viscous brown mass was dissolved in 50 c.c. of acetone, and the solution

poured into 500 c.c. of water. The curdy solid (m. p. 70—85°) which separated was dissolved in acetone, water added until a slight turbidity was produced, and the acetone allowed to evaporate spontaneously. The small needles (m. p. 175—185°) which crystallised out were again treated in the same way, and then melted at 202—208°. This substance (which weighed 0.07 gram) was probably very impure *as*-phenylcyanocarbamide (Found: N = 22.73.  $C_8H_7ON_2$  requires N = 26.09 per cent.).

Phenylcyanourethane was unaffected by heating with aqueous ammonia or saturating with ammonia in ethereal solution; it was completely decomposed by heating in a sealed tube with ammonium carbonate.

*Action of Nitrous Acid on as-Phenylbiuret.*—*as*-Phenylbiuret (McKee, *Amer. Chem. J.*, 1901, **26**, 254), dissolved in a large volume of water, gave no nitrogen on adding nitrous acid, and the resulting solution gave a pale yellow coloration with alkaline  $\beta$ -naphthol. After standing over-night with the nitrous acid, however, a pale red colour was produced by the  $\beta$ -naphthol. *s*-Diphenylcarbamide and *s*-acetylphenylcarbamide behaved in the same way, but phenylcarbamide gave nitrogen and a scarlet azo-colour.

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## CCXLVI.—*The Interchange of Alcohol Radicles in Esters. Part II.*

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THE present investigation, which is a continuation of that previously published (this vol., p. 883), was undertaken with the object of discovering the cause which determines the interchange of alcohol radicles in esters.

The reaction, which is probably reversible, is entirely inhibited in many cases, or, in other words, the alkyl group is too firmly attached to the oxygen atom to be removed by the action of even a large quantity of a second alcohol or its sodium compound.

From the summary of results given at the end of the paper, it is clear that the alkyl group in the esters is rendered more mobile by the proximity of acidic groups. A striking illustration is that of the neutral and acid esters of dibasic acids. Ethyl oxalate readily reacts with menthol, whereas the presence of one or more intervening hydrocarbon groups ( $CH_2$  or  $CH$ ), as in ethyl malonate, ethyl succinate, and methyl phthalate, prevents the interchange.

Interchange is, however, effected if one free carboxyl group is present, for all three acid esters of the above acids react. The  $\alpha$ -ketonic esters are all reactive; but the  $\beta$ -ketonic esters react only in those cases where a methylene group or a negatively substituted methylene group intervenes between the ketone and the ester group. When one or both hydrogen atoms of the methylene group are replaced by alkyl groups, as in the mono- and di-alkyl derivatives of acetoacetic ester, the action is again repressed.

Attention may be directed to the close resemblance between the inert character of the ester of the simple aliphatic acids and that of aromatic esters, as illustrated by hydroxybenzoic ester.

It should be pointed out that no deduction of a quantitative nature can be drawn from these experiments; for the very different volatility of the esters rendered it necessary to submit them to varying conditions of temperature and pressure during the reaction.

The mechanism of the interchange is still obscure and therefore we propose to continue the investigation and to examine, among other things, the effect of certain alcohols and their substitution products on the same ester.

#### EXPERIMENTAL.

*l*-Menthol and Ethyl Pyruvate.—9.1 Grams of ethyl pyruvate and 12.2 grams of *l*-menthol with 0.022 gram of sodium were heated at 130–140° for eight hours. In the course of heating, about 1 c.c. of liquid, chiefly ethyl alcohol, distilled. The product was fractionated under reduced pressure; the portion which distilled at 132–140°/14 mm. (1.9 grams) consisted chiefly of *l*-menthyl pyruvate (Cohen and Whiteley, T., 1901, 79, 1309; b. p. 136–140°/22 mm.; McKenzie, T., 1905, 87, 1380, b. p. 131–132°/10 mm.) and showed  $[\alpha]_D^{25} -60.8^\circ$  ( $c = 2.73$ ,  $l = 2$ ) in alcohol.

By the above treatment, besides the interchange of groups, some sort of complex condensation seemed to take place, giving rise to a considerable amount of tarry matter (3.6 grams) which had a very high boiling point.

*l*-Menthol and Ethyl Oxalacetate.—(I) Nine grams of ethyl oxalacetate and 15 grams of *l*-menthol with 0.022 gram of sodium were heated at about 90° under 10–30 mm. pressure for seven hours. After the reaction was finished, the excess of menthol and unchanged ethyl ester were expelled by distillation under 20 mm. pressure, the temperature of the metal-bath being raised to 175°. The remaining liquid was subjected to steam distillation in order to remove any trace of menthol, extracted with ether, and dried over calcium chloride. The ethereal solution showed  $\alpha_D -6.09^\circ$  in alcohol and gave 8.5 grams of a syrupy liquid on evaporation.

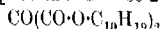
(II) A similar experiment was carried out, but without sodium. 5.2 Grams of a syrupy liquid were obtained from 9.6 grams of the ethyl ester, and showed  $[\alpha]_D^{25} -45.3^\circ$  ( $c = 2.68$ ,  $l = 2$ ) in alcohol.

As the esters of oxalacetic acid easily decompose into carbon monoxide and malonic ester at a high temperature (Wislicenus, *Ber.*, 1894, **27**, 793), the menthyl ester could not be isolated from the mixture containing the ethyl ester by the usual method of fractional distillation in a vacuum.

*l-Menthol and Ethyl Acetylpyruvate*.—Ten grams of ethyl acetylpyruvate and 10 grams of *l*-menthol were heated at  $155\text{--}165^\circ$  for three and a half hours, during which time 1.8 grams of ethyl alcohol distilled. The product was fractionated under reduced pressure, and the portion (6.3 grams) which distilled at  $175\text{--}190^\circ/16$  mm. gave, on refractionation, 3.6 grams of a colourless liquid boiling at  $185\text{--}192^\circ/12$  mm. and showing  $[\alpha]_D^{25} -72.3^\circ$  ( $c = 4.33$ ,  $l = 2$ ) in alcohol. It was found to be the menthyl ester of acetylpyruvic acid by analysis (Found: C = 67.02; H = 9.29.  $C_{15}H_{24}O_4$  requires C = 67.13; H = 9.02 per cent.).

A similar result was obtained by heating an equimolecular mixture of the ethyl ester and menthol with a little sodium at  $90^\circ$  under 10–30 mm. pressure for six hours.

*l-Menthol and Ethyl Mesoxalate*.—Twelve grams of ethyl mesoxalate and 18 grams of *l*-menthol with 0.028 gram of sodium were heated at  $90^\circ$  under 15–30 mm. pressure for six hours. The product was fractionated under diminished pressure; the fraction which boiled at  $171\text{--}200^\circ/13$  mm. (4.3 grams) deposited a considerable quantity of crystals on standing for three weeks. The crystalline mass was pressed on a porous plate, washed with water, and recrystallised from alcohol. The colourless microprisms thus obtained melted towards  $63^\circ$  and showed  $[\alpha]_D^{25} -58.6^\circ$ . It was apparently a mixture of the *l*-menthyl ester of mesoxalic acid and a small quantity of ethyl dihydroxymalonate, judging from the result of its analysis [Found: C = 60.2; H = 8.9.



requires C = 70.1; H = 9.6, whilst  $C(OH)_2(CO \cdot O \cdot C_2H_5)_2$  requires C = 43.8; H = 6.2 per cent.]. From the residue of fractional distillation under reduced pressure, a very small quantity of crystals, melting at  $67\text{--}68^\circ$ , was obtained which seemed to be menthyl oxalate formed by partial decomposition.

*l-Menthol and Ethyl Monoacetylmalonate*.—Five grams of ethyl monoacetylmalonate and 7.8 grams of *l*-menthol with 0.015 gram of sodium were heated at  $90^\circ$  under 10–30 mm. pressure for six hours. The product was distilled up to  $103^\circ/14$  mm. and the residue was subjected to steam distillation to remove all menthol, extracted



with ether, and dried over sodium sulphate. The ethereal solution gave a syrup after the ether had been removed, which solidified slowly to a crystalline mass when rubbed with a glass rod, with addition of a little alcohol, and cooled in ice. After recrystallisation from alcohol, *menthyl monoacetylmalonate* was obtained in colourless, long needles (0.8 gram) with m. p.  $58^{\circ}$  and showing  $[\alpha]_D^{25} -77.5^{\circ}$  ( $c = 1.18$ ,  $l = 2$ ) in alcohol (Found: C = 71.46; H = 10.32.  $C_{25}H_{42}O_6$  requires C = 71.04; H = 10.02 per cent.).

*l-Menthol and Ethyl Diacetylmalonate*.—Twelve grams of ethyl diacetylmalonate and 15.4 grams of *l*-menthol with 0.034 gram of sodium were heated at about  $90^{\circ}$  under 15–30 mm. pressure for five hours. The product was distilled up to  $115^{\circ}/18$  mm., and the residue was distilled with steam to remove menthol, extracted with ether, and dried over sodium sulphate. The oil obtained after the ether was driven off was again fractionated under diminished pressure. It was found to undergo decomposition at a higher temperature, apparently giving off acetic acid and some other gas. The portion which distilled at  $173$ – $195^{\circ}/16$  mm., smelling strongly of acetic acid and acid to litmus paper, showed  $[\alpha]_D^{25}$  about  $-26^{\circ}$  ( $c = 2.58$ ,  $l = 2$ ) in alcohol. By heating it at a higher temperature, menthol also seemed to be split off.

*l-Menthol and Ethyl Acetoxymalonate*.—An equimolecular mixture of ethyl acetoxymalonate and *l*-menthol with a little sodium was heated at about  $90^{\circ}$  under 15–30 mm. pressure for six hours. The product was distilled up to  $120^{\circ}/12$  mm. and the residue was subjected to steam distillation to remove menthol, during which distillation a slight decomposition took place, acetic acid being given off. The isolation of the menthyl ester was unsuccessful, but the residual oil, after extraction with ether and drying over sodium sulphate, showed  $[\alpha]_D^{25} -10.4^{\circ}$  ( $c = 10.2$ ,  $l = 2$ ) in alcohol.

*l-Menthol and Ethyl Phenoxymalonate*.—8.6 Grams of ethyl phenoxymalonate and 10.7 grams of *l*-menthol with 0.029 gram of sodium were heated at about  $90^{\circ}$  under 15–30 mm. pressure for seven hours. The reaction product was distilled up to  $107^{\circ}/16$  mm. and the residue was subjected to steam distillation to remove every trace of menthol. The oil, thus freed from menthol, solidified very slowly and, on repeated recrystallisation from alcohol, the *menthyl* ester was obtained in colourless micro-needles (1.5 grams) with m. p.  $96^{\circ}$ , and  $[\alpha]_D^{25} -55.5^{\circ}$  ( $c = 0.613$ ,  $l = 2$ ) in alcohol (Found: C = 73.56; H = 9.32.  $C_{19}H_{34}O_5$  requires C = 73.68; H = 9.39 per cent.).

*l-Menthol and Ethyl Methylene-malonate*,  $CH_2=C(CO_2Et)_2$ .—Two grams of ethyl methylenemalonate and 4.3 grams of *l*-menthol with a little sodium were heated at  $130$ – $150^{\circ}$  for seven hours.

The product was distilled with steam to remove all menthol, extracted with ether, and dried over sodium sulphate. The viscous liquid obtained from the ethereal solution showed  $[\alpha]_D^{20} -20.4^\circ$  ( $c = 1.37$ ,  $l = 2$ ) in alcohol.

A similar experiment was carried out under reduced pressure at  $90^\circ$ , and the product, after all the menthol had been removed by steam distillation, gave a levorotatory syrupy liquid.

The isolation of the pure menthyl ester was not successful in either case.

*l-Menthol and Ethyl Ethoxymethylenemalonate*,  $\text{OEt}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$ .

—Ten grams of ethyl ethoxymethylenemalonate and 14.5 grams of *l*-menthol with 0.026 gram of sodium were heated at about  $90^\circ$  under 10–30 mm. pressure for six and a half hours. The product was fractionated under diminished pressure, and the portion which distilled at  $185\text{--}224^\circ$  (mainly  $215\text{--}220^\circ/12$  mm.) gave, on redistillation, a colourless, viscous oil (3.9 grams) with b. p.  $215\text{--}221^\circ/10$  mm. and  $[\alpha]_D^{25} -39.6^\circ$  ( $c = 2.16$ ,  $l = 2$ ) in alcohol. This oil was found to be the *l*-menthyl ester, containing a little unchanged ethyl ester (Found: C = 68.30; H = 9.98.  $\text{C}_{26}\text{H}_{44}\text{O}_5$  requires C = 71.51; H = 10.16 per cent.).

*l-Menthol and Ethyl Hydroxymethylenemalonate*.—6.1 Grams of ethyl hydroxymethylenemalonate and 10.1 grams of *l*-menthol with 0.021 gram of sodium were heated at  $80\text{--}90^\circ$  under 20–30 mm. pressure for six hours. The product distilled mostly below  $145^\circ/17$  mm. The small remaining quantity of oil was distilled with steam to remove any menthol and the residue was extracted with ether. The dried ethereal solution showed a very small rotation of  $\alpha_D -0.28^\circ$  in alcohol. It is rather doubtful if the interchange of groups had actually taken place in this case, and if so, it must have been to a very small extent.

*l-Menthol and Ethyl Hydrogen Malonate*.—10.6 Grams of ethyl hydrogen malonate and 12.5 grams of *l*-menthol with 0.026 gram of sodium were heated at about  $90^\circ$  under 15–30 mm. pressure for five hours. The product was distilled with steam to remove menthol and the residue was extracted with ether. The ethereal extract gave a small quantity of viscous oil, which was dissolved in a dilute solution of sodium carbonate; after the solution had been extracted with ether to remove any insoluble matter, the oil was reprecipitated by the careful addition of acetic acid. The oil thus obtained showed  $[\alpha]_D^{20} -46.8^\circ$  ( $c = 1.54$ ,  $l = 2$ ) in alcohol and consisted undoubtedly of the menthyl ester formed by interchange of the ethyl group.

*l-Menthol and Methyl Hydrogen Succinate*.—Ten grams of methyl hydrogen succinate and 11.9 grams of *l*-menthol with 0.03 gram

of sodium were heated at 90–100° under 17–20 mm. pressure for five hours. The product was distilled up to 150°/20 mm. and the remaining syrupy oil was dissolved in a warm dilute solution of sodium carbonate. The solution was extracted with ether to remove any impurity, the oil, reprecipitated by careful addition of acetic acid, was distilled with steam to remove any trace of menthol and the excess of acetic acid. The residue was extracted with ether and dried over sodium sulphate. The ethereal extract gave a little oil, which, after three weeks' standing at the ordinary temperature, solidified to a crystalline mass. On recrystallisation from alcohol, the substance was obtained in colourless prisms, m. p. 57–59°, showing  $[\alpha]_D^{25} -61.0^\circ$  ( $c = 0.50$ ,  $l = 2$ ) in alcohol. It was found to be the *menthyl hydrogen* ester of succinic acid by analysis (Found: C = 65.23; H = 9.66.  $C_{14}H_{24}O_4$  requires C = 65.58; H = 9.44 per cent.).

*l-Menthol and Ethyl o-Nitrobenzoate.*—Ten grams of ethyl *o*-nitrobenzoate and 8 grams of *l*-menthol with 0.04 gram of sodium were heated at about 90° under 10–30 mm. pressure for five and a half hours. A vigorous reaction was observed at the beginning of heating. The product was distilled up to 202°/13 mm., and the residual dark syrupy mass (3.2 grams) was dissolved in alcohol and boiled with animal charcoal for one hour and filtered hot. The menthyl ester separated in an oily state at first, but on seeding, it solidified at once. When recrystallised from alcohol, it was obtained in large, colourless prisms (2.6 grams), m. p. 64–65°, showing  $[\alpha]_D^{25} -152.2^\circ$  ( $c = 1.58$ ,  $l = 2$ ) in alcohol. It was found to be identical with the menthyl ester formerly obtained by Cohen and Armes (T., 1905, **87**, 1190) by a direct synthesis.

*l-Menthol and Ethyl m-Nitrobenzoate.*—Ten grams of ethyl *m*-nitrobenzoate and 8 grams of *l*-menthol with 0.04 gram of sodium were treated in the same way as the ortho-compound. The product was fractionated under diminished pressure; the portion which distilled at 223–224°/13 mm. gave, on redistillation, a pale greenish-yellow, viscous oil (6.4 grams) with a weak fluorescence, boiling at 228°/10 mm. and showing  $[\alpha]_D^{25} -77.5^\circ$  ( $c = 1.58$ ,  $l = 2$ ) in alcohol. It was found to be identical with the menthyl ester of *m*-nitrobenzoic acid obtained directly by Cohen and Armes (*loc. cit.*).

*l-Menthol and Ethyl p-Nitrobenzoate.*—Ten grams of ethyl *p*-nitrobenzoate and 8 grams of *l*-menthol with 0.04 gram of sodium were treated in the same way as its isomerides. The product was distilled up to 210°/12 mm. The residue, which solidified on cooling, was dissolved in alcohol, boiled with animal charcoal for one and a half hours, and filtered hot. On cooling, almost colourless

crystals of menthyl *p*-nitrobenzoate (7.5 grams) were obtained, m. p.  $63^{\circ}$ ,  $[\alpha]_D^{25} -75.0^{\circ}$  ( $c = 1.58$ ,  $l = 2$ ) in alcohol. The substance was identical with that prepared by Cohen and Armes (*loc. cit.*).

*l*-Menthol and Ethyl *m*-Aminobenzoate.—Eight grams of ethyl *m*-aminobenzoate and 7.6 grams of *l*-menthol with 0.032 gram of sodium were heated at  $90^{\circ}$  under 10–30 mm. pressure for five hours, and the product was fractionated. The portion which distilled above  $200^{\circ}/16$  mm. (1.6 grams), when dissolved in alcoholic hydrochloric acid, solidified after some time to a colourless, crystalline mass, which, after being pressed on a porous plate, was recrystallised from alcohol, containing a little hydrogen chloride, and was obtained in colourless prisms, melting indefinitely towards  $190^{\circ}$ , and showed  $[\alpha]_D^{25} -72.9^{\circ}$  ( $c = 0.288$ ,  $l = 2$ ) in alcohol. It was undoubtedly the hydrochloride of menthyl *m*-aminobenzoate (Found: Cl = 12.06.  $C_{17}H_{25}O_2N \cdot HCl$  requires Cl = 11.37 per cent.) containing probably a very small quantity of the hydrochloride of the unchanged ethyl ester.

*l*-Menthol and Methyl Hydrogen Phthalate.—Ten grams of methyl hydrogen phthalate and 8.7 grams of *l*-menthol with 0.022 gram of sodium were heated at about  $90^{\circ}$  under 15–30 mm. pressure for six and a half hours. The dark syrupy product was directly distilled with steam to remove menthol. When the contents of the flask were evaporated on a water-bath, a solid, consisting of fine prisms, separated with some oil which also solidified when cooled. The whole, which was evidently a mixture of two products, was filtered and the two substances were separated mechanically from one another. The crystals with the higher m. p. (6.5 grams) were found to be chiefly phthalic acid, which was obtained in a pure state [4.8 grams; m. p.  $210$ – $211^{\circ}$  (decomp.)] by recrystallisation from a large bulk of hot water. In order to ascertain the origin of this phthalic acid, methyl hydrogen phthalate alone was heated with water at  $100^{\circ}$  for several hours, and was found to decompose very readily into phthalic acid and methyl alcohol.

Although the monomethyl ester was so easily hydrolysed with water, the corresponding menthyl ester survived steam distillation, and the product with the lower m. p. (2.9 grams) was found to be the crude menthyl ester. It was dissolved in a hot dilute solution of sodium carbonate, filtered, extracted with ether to remove any impurity, and the acid menthyl ester was reprecipitated by careful addition of acetic acid. It was obtained in colourless micro-needles, m. p.  $110^{\circ}$  (2.7 grams), showing  $[\alpha]_D^{25} -102.3^{\circ}$  ( $c = 0.988$ ,  $l = 2$ ) in benzene; Arth (*Ann. Chim. Phys.*, 1886, [vi], 7, 485) found  $[\alpha]_D^{25} -105.55^{\circ}$ , and Cohen, Woodroffe, and Anderson (*T.*, 1916, 109, 230) found  $[\alpha]_D^{25} -109.32^{\circ}$  in the same solvent.

*l*-Menthol and Methyl Terephthalate; *l*-Menthol and Methyl Hydrogen Terephthalate.—Owing to their high m. p. and their insolubility in fused menthol, these methyl esters proved unsuitable for our experiments.

The Interchange of Alcohol Radicles in Esters. Replacement of an Alkyl Group by the *l*-Menthyl Group.

Alkyl esters of monobasic aliphatic acid derivatives.	Ethyl acetate .....	—
	„ bromoacetate .....	—
	„ $\alpha$ -cyanopropionate .....	—
	Methyl phenylacetate .....	+
	Ethyl phenylacetate .....	+
	Methyl phenylchloroacetate .....	+
	„ phenylbromoacetate .....	—
	„ $\alpha$ -bromo- $\beta$ -phenylpropionate .....	—
	Ethyl trichloroacetate .....	—
	„ atrolactinate .....	—
	„ $\alpha$ -cyano- $\beta$ -phenylpropionate .....	—
	Ethyl cinnamate .....	—
Alkyl ester of unsaturated aliphatic acid.		
Alkyl esters of $\alpha$ -ketonic acids.	Ethyl acetoacetate .....	+
	„ methylacetoacetate .....	+
	„ methylethylacetoacetate .....	—
	Ethyl pyruvate .....	+
	„ oxalacetate .....	+
	„ acetylpyruvate .....	+
	„ mesoxalate .....	+
	Ethyl oxalate .....	+
	„ malonate .....	—
Neutral alkyl esters of dibasic aliphatic acids.	„ succinate .....	—
	Ethyl monoacetylmalonate .....	+
	„ diacetylmalonate .....	+
	„ monobromoacetate .....	—
	„ acetoxy-malonate .....	+
	„ phenoxy-malonate .....	+
	„ mononitromalonate .....	—
	„ methylenemalonate .....	+
	„ allylmalonate .....	—
	„ ethoxymethylenemalonate .....	+
	„ hydroxymethylenemalonate .....	?
	Ethyl hydrogen malonate .....	+
	Methyl hydrogen succinate .....	+
Acid alkyl esters of dibasic aliphatic acids.		
Alkyl esters of benzoic acid derivatives.	Ethyl benzoate .....	+
	Methyl <i>o</i> -toluate .....	—
	„ <i>m</i> -toluate .....	+
	„ <i>p</i> -toluate .....	—
	Ethyl <i>o</i> -nitrobenzoate .....	+
	„ <i>m</i> -nitrobenzoate .....	+
	„ <i>p</i> -nitrobenzoate .....	+
	„ <i>o</i> -aminobenzoate .....	—
	„ <i>m</i> -aminobenzoate .....	+
	„ <i>p</i> -aminobenzoate .....	—
	Methyl salicylate .....	—

Alkyl ester of hydrogenated benzoic acid.	Ethyl <i>cyclohexanecarboxylate</i> .....	—
Acid and neutral alkyl esters of benzenedicarboxylic acids.	Methyl hydrogen phthalate .....	+
	„ phthalate .....	—
	„ hydrogen terephthalate .....	?
	„ terephthalate .....	?

*Note.*—The names in italics are those of substances referred to in the previous paper.

#### *Summary of the Results.*

(I) The acid nature of an alkyl ester seems to promote the interchange of groups. The introduction of the following groups generally helps the reaction: phenyl, acetyl, acetoxy, phenoxy, carboxyl, nitro.

(II) Introduction of halogens does not materially influence the interchange.

(III) In some cases, a double bond assists the reaction.

(IV) Most of the esters of  $\alpha$ -ketonic acids undergo interchange, due, undoubtedly, to the presence of the carbonyl group in the  $\alpha$ -position to the carboxyl group.

(V) Introduction of the hydroxyl group is not favourable to the interchange.

(VI) In the case of esters of benzoic acid derivatives, *o*- and *p*-compounds behave similarly, but differ from the *m*-compound.

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### CCXLVII.—*Studies in the Anthracene Series. Part III.*

By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and  
HERBERT HENRY GRAINGER.

IN a former communication (T., 1921, **119**, 901), it was shown that a pyridinium salt is formed when anthracene, suspended in pyridine, is treated with bromine, the reaction in this case consisting in the addition of bromine to the *meso*-carbon atoms and simultaneous formation of the quaternary salt. It was considered desirable to extend the study of this type of reaction, and in Part II of this series (this vol., p. 1376) it was shown that pyridinium salts can be obtained from certain hydroxyanthraquinones, in which the hydroxyl groups are in the *ortho*- or *para*-position to one another, by the simultaneous action of bromine and pyridine, although in the compounds thus obtained the pyridinium groups are, of course, attached to the benzene rings.

The present communication describes experiments undertaken in

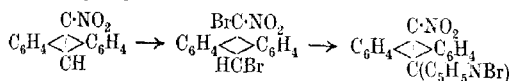
order to study the influence of substituents attached to the *meso*. carbon atoms on the formation of pyridinium salts by bromination in the presence of pyridine.

The action of bromine on 9:10-dibromoanthracene has been studied by several investigators (Graebe and Liebermann, *Annalen*, 1870, Suppl. VII, 304; Kaufler and Imhoff, *Ber.*, 1904, **37**, 4706; Kurt Meyer and Zahn, *Annalen*, 1913, **396**, 166). Graebe and Liebermann found that, although more highly brominated compounds could not be obtained from 9:10-dibromoanthracene by the action of bromine in carbon disulphide solution, a dibromoanthracene tetrabromide was easily obtained by exposing 9:10-dibromoanthracene to bromine vapour at the ordinary temperature without the use of a solvent. The tetrabromide thus obtained loses hydrogen bromide very readily when heated and passes into 2:9:10-tribromoanthracene. It has recently been reinvestigated by Battegay and Claudin (*Bull. Soc. chim.*, 1921, [iv], **29**, 1022) and Grandmougin (*Compt. rend.*, 1921, **173**, 1176), who have proved it to be 1:2:3:4:9:10-hexabromo-1:2:3:4-tetrahydroanthracene. Kurt Meyer and Zahn, on the other hand, treated 9:10-dibromoanthracene with bromine in the presence of a little chloroform and obtained a dibromoanthracene tetrabromide which differed widely in its physical properties from the compound obtained by Liebermann and Graebe, but which, on heating, also gave 2:9:10-tribromoanthracene. They attribute the difference to geometrical isomerism and have obtained similar isomerides by brominating 9:10-dichloroanthracene. The marked difference in the behaviour of dibromoanthracene towards bromine without a solvent or in the presence of chloroform or carbon disulphide rendered an investigation of its behaviour towards bromine in pyridine solution a matter of considerable interest. Repeated experiments have been made, but in every case negative results have been obtained, the whole of the original material being recovered unchanged. Similar negative results were also obtained when 9:10-dichloroanthracene was submitted to the simultaneous action of bromine and pyridine.

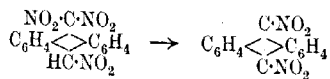
At this point it may be mentioned that the dibromoanthracene tetrabromide of Graebe and Liebermann, when treated with pyridine, forms a small amount of a pyridinium salt, although the main reaction consists in the removal of hydrogen bromide and the formation of tribromoanthracene. This reaction is being further examined in connexion with a series of experiments which are being carried out in these laboratories on the action of pyridine and other organic bases on the haloids of aromatic hydrocarbons, and therefore it is thought best to reserve further discussion on the nature of the product for a future communication.

When 9 : 9 : 10 : 10-tetrachloro-9 : 10-dihydroanthracene (anthraquinone tetrachloride) is warmed with pyridine, a deep red substance is formed (compare D.R.-P. 283,106), but owing to its refusal to crystallise it has not been found possible to obtain the substance in the pure condition. The deep red colour, however, suggests that opening of the pyridine ring has taken place with the formation of an anil of glutaconaldehyde (compare Zincke, *Annalen*, 1904, **330**, 361; **333**, 296; 1905, **338**, 107; **341**, 365; Zincke and Krollpfeiffer, *ibid.*, 1914, **408**, 285; Zincke and Weisspfenning, *J. pr. Chem.*, 1910, [ii], **82**, 1; 1912, [ii], **85**, 207; Barnett and Cook, *T.*, 1921, **119**, 908).

When 9-nitroanthracene is submitted to the combined action of bromine and pyridine, it is readily converted into 9-nitroanthranyl-10-pyridinium bromide, and salts of the same base are obtained by nitrating anthranyl-9-pyridinium nitrate. The production of a pyridinium salt is probably due to the intermediate formation of a dibromide and subsequent simultaneous pyridinium salt formation and loss of hydrogen bromide :



and this view of the mechanism of the reaction receives support from the fact that the action of pyridine on 9-chloro(or bromo)-10-nitro-9 : 10-dihydroanthracene consists solely in the removal of halogen acid, no trace of a pyridinium salt being produced. Pyridine appears to have a very considerable tendency to convert dihydroanthracene derivatives into anthracene derivatives, as even in the cold it at once removes nitrous acid from 9 : 9 : 10-trinitro-9 : 10-dihydroanthracene and converts it almost quantitatively into 9 : 10-dinitroanthracene. In fact, pyridine is a more convenient reagent to use for this purpose than the dilute sodium hydroxide recommended by Meisenheimer and Connerade (*Annalen*, 1904, **330**, 167).



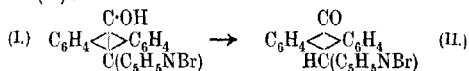
In view of these reactions, it is rather surprising that anthracene dibromide reacts with pyridine to form 9 : 10-dihydroanthranyl-9 : 10-dipyridinium dibromide and not anthranylpyridinium bromide (Barnett and Cook, *loc. cit.*).

If 9-nitroanthracene is brominated in carbon tetrachloride solution, a different reaction takes place and bromination is accompanied by the simultaneous displacement of the nitro-group, 9 : 10-dibromoanthracene being obtained.

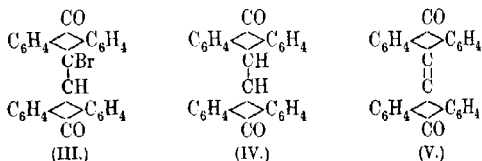


9:10-Dinitroanthracene does not react with bromine either in pyridine solution or in the presence of carbon tetrachloride.

9-Bromoanthrone reacts easily with pyridine to form a pyridinium salt, and this may have either the enolic structure (I) or the ketonic structure (II) :



Kurt Meyer and Sander (*Annalen*, 1913, **396**, 140) have shown that nearly all anthrone derivatives are almost completely enolised in pyridine solution, so that the former structure is the more probable. It is true that the compound is not fluorescent, but in this case the absence of fluorescence cannot be used as an argument for the absence of the "bridge" bond, as it has been shown in Part I of this series that the pyridinium group has a powerful influence in hindering fluorescence. It is doubtful whether this influence is due to the quinquivalent nitrogen atom or to the pyridine ring system, and in the hope of elucidating this point experiments were initiated with a view to prepare other quaternary salts derived from anthrone. These have failed to accomplish their object, as it has been found that, with the exception of pyridine, tertiary amines do not react with bromoanthrone to form quaternary salts. Thus, if a chloroform solution of bromoanthrone is treated with triethylamine, tripropylamine, tri-*isobutyl*amine, triamylamine,  $\alpha$ -picoline, or quinoline, a reaction takes place at once, but a quaternary salt is not formed, the product being bromodianthrone (III). In this respect, the tertiary amines resemble ammonia, as Kurt Meyer and Sander (*loc. cit.*) obtained bromodianthrone by treating bromoanthrone in benzene solution with ammonia, and the same reaction takes place when chloroform is substituted for benzene as a solvent. It is remarkable that whereas pyridine gives the quaternary salt, such a salt cannot be obtained from either  $\alpha$ -picoline or quinoline. Tribenzylamine does not react with bromoanthrone at the ordinary temperature.



Diethylamine resembles the tertiary amines in so far that it causes the loss of hydrogen bromide from two molecules of bromoanthrone. The product in this case, however, is not bromo-

dianthrone but dianthraquinone (V), two molecules of hydrogen bromide having been lost. These must be lost simultaneously, as dianthraquinone is not formed from bromodianthrone and diethylamine under the experimental conditions employed (cold chloroform solution), although, on prolonged heating, almost any amine will convert bromodianthrone into dianthraquinone, tertiary amines having, apparently, no tendency to form quaternary salts. Even pyridine fails to form a quaternary salt with bromodianthrone. The behaviour of diethylamine is exceptional and may be due to the fact that it is much more strongly basic than most aliphatic amines (Bredig, *Z. physikal. Chem.*, 1894, **13**, 294; Moore and Winnill, *T.*, 1912, **101**, 1651).

Other secondary amines, dimethylamine, methylaniline, benzylaniline, and piperidine, bring about a different type of reaction, bromine being split off as such and dianthrone (IV) formed. Methylamine and dimethylaniline also behave in this manner. The bromine liberated oxidises part of the bromoanthrone to anthraquinone, and this is always found among the reaction products. That the formation of dianthrone is actually due to the liberation of bromine is easily demonstrated by carrying out the reaction in the presence of an iodide, as iodine is then liberated and can be recognised by any of the usual tests. The experiment is particularly striking when dimethylaniline is employed.

Numerous descriptions of the preparation of dichloroanthracene by the chlorination of anthracene are to be found in the literature (Perkin, *Bull. Soc. chim.*, 1877, [ii], **27**, 464; Graebe and Liebermann, *Annalen*, 1870, Suppl. VII, 257; *Ber.*, 1868, **1**, 186; Schwarzer, *ibid.*, 1877, **10**, 376; Hammerschlag, *ibid.*, 1886, **19**, 1106; Kurt Meyer and Zahn, *loc. cit.*; D.R.-P. 283106; 284790), but none of them is well adapted to the preparation of the pure substance owing to the simultaneous formation of more highly chlorinated products. In the patent literature (D.R.-P. 289133), it is claimed that dichloroanthracene is formed when anthracene is treated with a very large excess of sulphuryl chloride, but the experimental details given are very scanty and on attempting to carry out the experiment by this means a dark-coloured product, which was very difficult to purify, was invariably obtained. By using much less sulphuryl chloride than that recommended in the patent and by employing carbon tetrachloride as a diluent, a method was finally worked out which gave a very pure product in good yield. Chlorination under these conditions seems to be preceded by the formation of an additive compound, as during the reaction, which is carried out at the ordinary temperature, the anthracene first dissolves to form a clear solution, and then the dichloroanthra-

cene crystallises out. In view of the fact that another investigator (Silberrad, T., 1921, **119**, 2029; this vol., p. 1015) is at present engaged in a systematic examination of the chlorination of the aromatic hydrocarbons by means of sulphuryl chloride, the mechanism of the reaction has not been further studied. In the case of anthracene, however, no catalyst is necessary, although the reaction is somewhat accelerated by the addition of a little sulphur chloride.

#### EXPERIMENTAL.

**9-Nitroanthracene.**—Anthracene, suspended in glacial acetic acid, was treated with the calculated amount of nitric acid according to the directions given by Dimroth (*Ber.*, 1901, **34**, 221) and Meisenheimer and Connerade (*Annalen*, 1904, **330**, 133). The solution was then treated with fuming hydrochloric (or hydrobromic) acid, and the precipitated chloro(or bromo)-nitrodihydroanthracene collected, washed, dried, and suspended in pyridine. The product consisted of 9-nitroanthracene and no pyridinium salt could be detected.

**9-Nitroanthranyl-10-pyridinium Bromide.**—(a) 9-Nitroanthracene (10 grams) was made into a thin cream with pyridine, and 7.5 c.c. of bromine were slowly added, the whole being well stirred and cooled in a freezing mixture. After keeping for two days at the ordinary temperature, the precipitate was collected with the aid of the pump, washed with pyridine and ether, and finally recrystallised first from water and then from absolute alcohol (Found: Br = 19.3.  $C_{19}H_{17}O_2N_2Br \cdot 2H_2O$  requires Br = 19.2 per cent.). (b) Anthranylpseudopyridinium bromide (25 grams) was dissolved in boiling water, and the hot solution treated with a solution of 12 grams of silver nitrate.\* The silver bromide was removed and the filtrate evaporated to dryness on the water-bath. The crude nitrate thus obtained was recrystallised from a mixture of alcohol and ether and then formed pale yellow plates which commenced to decompose at about 190° and finally melted at 221–222° (yield 20 grams) (Found: N = 8.96.  $C_{19}H_{14}O_3N_2$  requires N = 8.81 per cent.). The nitration was effected by adding 15 grams of the above nitrate slowly to 25 c.c. of concentrated sulphuric acid. After keeping at the ordinary temperature for three hours, the solution was poured on crushed ice, and the precipitate washed and recrystallised from hot water (Found: S = 7.75.  $C_{19}H_{14}O_6N_2S \cdot H_2O$  requires S = 7.69 per cent.). 9-Nitroanthranyl-10-pyridinium hydrogen sulphate forms a yellow, crystalline powder which does not melt below 300°. It is rather sparingly soluble in water or alcohol. The cold aqueous

\* If lead nitrate is used, a double salt with lead bromide is obtained.

solution at once gives a dark red precipitate when treated with dilute sodium hydroxide solution; in this respect the nitroanthranilpyridinium salts differ from the un-nitrated substances. When treated with aniline, a red solution is formed in the cold and the colour deepens on warming, but it was not found possible to isolate any pure substance. The *dichromate*, obtained by treating an aqueous solution of the sulphate with potassium dichromate, crystallises from boiling water in glistening, orange leaflets which fall to a yellow powder when dried [Found: Cr = 12.2.  $(C_{19}H_{13}O_2N_2)_2Cr_2O_7 \cdot 2H_2O$  requires Cr = 12.17 per cent.]. The *chloride* was obtained by treating the hydrogen sulphate with barium chloride and hydrochloric acid. It crystallised from water in golden-yellow leaflets. For analysis, a sample was recrystallised from alcohol (Found: Cl = 9.55.  $C_{19}H_{13}O_2N_2Cl \cdot 2H_2O$  requires Cl = 9.54 per cent.). The *nitrate* was obtained from the hydrogen sulphate by means of barium nitrate. It crystallised from hot water in golden-yellow plates which fell to a yellow powder on drying (Found: N = 11.18;  $H_2O$  = 2.59.  $C_{19}H_{13}O_5N_3 \cdot \frac{1}{2}H_2O$  requires N = 11.29;  $H_2O$  = 2.59 per cent.). The *picrate* was obtained as a yellow precipitate when an aqueous solution of the hydrogen sulphate or bromide was treated with picric acid. It was recrystallised from boiling water, in which it is very sparingly soluble, and then formed yellow needles which melted at  $261-263^\circ$  (Found: N = 13.3.  $C_{25}H_{15}O_9N_5$  requires N = 13.2 per cent.).

*Dibromoanthracene*.—9-Nitroanthracene (4.4 grams) was boiled under reflux for three hours with bromine (3.2 grams) and carbon tetrachloride (20 c.c.). Nitrogen peroxide was evolved. The product was recrystallised three times from glacial acetic acid and was then found to contain bromine, but no nitrogen. It melted at  $218^\circ$ , and the melting point was not changed by mixing it with pure dibromoanthracene.

*Dinitroanthracene*.—Trinitrodihydroanthracene was prepared by passing nitrogen peroxide into a chloroform solution of 9-nitroanthracene (Meisenheimer and Connerade, *loc. cit.*). When this was treated with about four parts of cold pyridine, it was almost at once converted into 9:10-dinitroanthracene, and this was found to be the most convenient method of obtaining the dinitro-compound. Dinitroanthracene remained unattacked when boiled with bromine in carbon tetrachloride solution. It was also unaffected by treatment with bromine in cold pyridine solution.

*9-Hydroxyanthranil-10-pyridinium Bromide (I) or Anthronilpyridinium Bromide (II)*.—(a) To a solution of bromoanthrone (8.5 grams) in 150 c.c. of chloroform cooled in ice, pyridine (3 c.c.) was added and the whole kept at  $0^\circ$  for two hours. The precipi-

tate was collected, washed with chloroform, and recrystallised from boiling water.

(b) The following method is more convenient for preparing the above bromide. Bromoanthrone (10 grams) is heated on the water bath for fifteen minutes with pyridine (80 c.c.). After cooling, the precipitate is collected, washed with pyridine and ether, and recrystallised from dilute hydrobromic acid. For analysis, a sample was recrystallised three times from alcohol and ether; it then formed pale yellow needles which melted with profound decomposition at  $185-188^{\circ}$  (Found: C = 63.5; H = 5.55; N = 3.77; Br = 22.5.  $C_{19}H_{14}ONBr \cdot \frac{1}{2}H_2O$  requires C = 63.2; H = 4.16; N = 3.88; Br = 22.2 per cent.).

This bromide is easily soluble in hot water or alcohol, but is sparingly soluble in the cold. On prolonged boiling with water, it is converted into anthraquinone, but hydrolysis takes place rapidly when the cold solution is treated with sodium nitrite or sodium acetate. The product thus obtained probably contains nitroanthrone, but owing to the presence of impurities it was not found possible to obtain it in a state of purity. Aqueous solutions of the bromide give deep red colorations with ammonia and sodium hydroxide. This is almost certainly due to the opening of the pyridine ring, but owing to the uninviting physical properties of the substance formed, it was not further investigated. Highly coloured products are also obtained by heating the substance with aniline. The nitrate was obtained by treating a boiling solution of the bromide with one equivalent of silver nitrate. After the silver bromide had been removed, the filtrate was cooled, when the nitrate crystallised out; it was purified by recrystallisation from alcohol containing a little ether. It is much less soluble than the bromide (Found: N = 8.23.  $C_{19}H_{14}O_4N_2$  requires N = 8.38 per cent.).

#### *Action of Ammonia and Amines on Bromoanthrone.*

To save space it will be best to state the standard conditions used and merely to note under the individual amines when it was found necessary to modify these. Bromoanthrone (5 grams) was dissolved in chloroform (50 c.c.), and the cold solution treated with the amine (2 to 5 c.c.). After keeping at the ordinary temperature for two hours, the solution was diluted with about twice its volume of ether and the precipitate collected and washed with dilute hydrobromic acid. The final purification of the product was effected by recrystallisation from xylene or from a mixture of chloroform and light petroleum or from both these solvents.

The products of the reactions were tested for bromine and nitro-

gen and were identified by the method of mixed melting points and by their colour reactions with concentrated sulphuric acid, with and without the addition of a drop of nitric acid. Thus anthrone, bromoanthrone, and dianthrone all give yellow solutions in concentrated sulphuric acid which are turned red by the addition of a drop of nitric acid. Bromodianthrone gives a bluish-green solution in concentrated sulphuric acid, the colour changing to red on the addition of nitric acid. Dianthraquinone gives a bordeaux-red solution in concentrated sulphuric acid and the colour is not changed by the addition of a drop of nitric acid. Dianthraquinone is also easily recognised by its giving a green solution in boiling xylene, the colour gradually fading to yellow as the solution cools, and by the fact that the crystals turn green when pressed. In addition to the above colour reactions, the behaviour of bromodianthrone with pyridine is characteristic. The solution in the cold solvent is almost colourless, but on heating becomes first violet, then blue, and finally green. On cooling the green solution, the colour fades to yellow and crystals of dianthraquinone are deposited. Dianthrone is very easily characterised by the fact that it crystallises unchanged from boiling concentrated nitric acid; in fact, recrystallisation from this solvent is the best method of obtaining small amounts of the pure substance, although the sparing solubility renders the method unsuitable to the treatment of larger quantities. When purified by this method, dianthrone is quite colourless and not yellow, as usually obtained from other solvents.

*Ammonia*.—Dry ammonia gas was used and ammonium bromide commenced separating almost at once. The product was bromodianthrone. More satisfactory results are obtained by this method than by using benzene as a solvent (Kurt Meyer and Sander, *loc. cit.*).

*Methylamine*. *Dimethylamine*.—Potassium hydroxide was added to an aqueous solution of the base, and the solution then warmed. The gas evolved was dried by means of soda-lime and solid potassium hydroxide. In both cases the product consisted of dianthrone.

*Diethylamine*.—The product was dianthraquinone.

*Triethylamine*. *Tripropylamine*. *Triamylamine*.—The products were bromodianthrone.

*Triisobutylamine*.—No reaction took place under standard conditions, and the reaction was only complete after boiling for five hours. The product was bromodianthrone.

*Piperidine*.—The reaction was rapid and was complete after thirty minutes. The product was dianthrone.

*Methylaniline*. *Dimethylaniline*.—In both cases, the products were dianthrone.

*Benzylaniline*.—The reaction was very slow. After three days, some dianthrone was obtained.

*Tribenzylamine*.—No reaction was observed under standard conditions, and the reaction was very slow even on prolonged boiling.

*$\alpha$ -Picoline*.—The reaction was allowed to proceed at the ordinary temperature over-night. On adding ether, a pasty precipitate was obtained which became solid when warmed with dilute hydrobromic acid. On recrystallising, pure bromodianthrone was obtained.

*Quinoline*.—The reaction was allowed to proceed at the ordinary temperature over-night. On adding ether, a sandy, brown precipitate was obtained. This was washed with alcohol and recrystallised from xylene, when pure bromodianthrone was obtained.

#### *Preparation of 9:10-Dichloroanthracene.*

Technical refined anthracene (about 95 per cent.; 90 grams) was suspended in 650 c.c. of carbon tetrachloride, and 135 c.c. of sulphuryl chloride were added. The flask was then closed by means of a calcium-chloride tube and the whole kept at the ordinary temperature. After a few minutes, evolution of gas commenced and the anthracene slowly passed into solution, the whole dissolving in about four hours. The clear orange-yellow solution thus obtained was kept for a further period of twenty-four hours, when a further evolution of gas took place and dichloroanthracene crystallised out. After cooling in ice, the precipitate was collected, washed with carbon tetrachloride, and finally recrystallised from the same solvent. The product melted sharply at 209°. The yield was almost theoretical.

#### *Summary.*

(i) Bromine in pyridine solution does not react with 9:10-dichloroanthracene, 9:10-dibromoanthracene or 9:10-dinitroanthracene.

(ii) A pyridinium salt is obtained when 9-nitroanthracene is treated with bromine in the presence of pyridine, and salts of the same base are obtained by nitrating anthranilpyridinium nitrate.

(iii) 9-Nitroanthracene, when brominated in carbon tetrachloride solution, gives 9:10-dibromoanthracene, owing to the displacement of the nitro-group.

(iv) Pyridine converts chloronitrodihydroanthracene into 9-nitroanthracene, and trinitrodihydroanthracene into dinitroanthracene.

(v) The action of amines on bromoanthrone has been studied and it has been found that bromodianthrone, dianthrone, or dianthraquinone is formed, the product obtained depending on the amine used.

(vi) A simple method of preparing pure 9 : 10-dichloroanthracene in almost theoretical yield from anthracene and sulphuryl chloride has been worked out.

In conclusion, the authors desire to express their thanks to the South Metropolitan Gas Co. for the supply of anthracene and pyridine, to British Dyestuffs Corporation, Ltd., for a gift of dimethylamine, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this research.

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### CCXLVIII.—*Inorganic Complex Salts. Crystallographic and Optical Study. Part I.*

By ISABEL ELLIE KNAGGS.

THE crystals of the inorganic complex salts now to be described were prepared in the Cambridge University Chemical Laboratory by Mr. W. Thomas, who will shortly communicate an account of their preparation.

The crystals were extremely difficult to obtain and were for the most part very small and poorly developed. Their crystallographic and optical determination has for this reason proved a difficult task.

The following salts have been investigated: (1) Potassium ferri-oxalate +  $3\text{H}_2\text{O}$ ; (2) potassium aluminium oxalate +  $3\text{H}_2\text{O}$ ; (3) ammonium *cis*-diamminodinitro-oxalatocobaltate +  $\text{H}_2\text{O}$ ; (4) ammonium *trans*-diamminodinitro-oxalatocobaltate +  $\text{H}_2\text{O}$ ; (5) potassium *cis*-diamminodinitro-oxalatocobaltate +  $\text{H}_2\text{O}$ ; (6) potassium *trans*-diamminodinitro-oxalatocobaltate +  $\text{H}_2\text{O}$ ; (7) barium *cis*-diamminodinitro-oxalatocobaltate +  $3\text{H}_2\text{O}$ ; (8) ammonium diamminotetranitrocobaltate.

So far only racemic compounds have been examined, all attempts to crystallise the optically active components having failed, owing to racemisation taking place during crystallisation.

The compounds (1) and (2) crystallise in the holohedral class of the monoclinic system and are isomorphous with each other. The *cis*-compounds, (3), (5), and (7), were found to show a close isomorphism and to belong to the ditrigonal-scalenohedral class of the rhombohedral system. The *trans*-compounds, (4) and (6), although they show close resemblances in the values of their crystal



angles and crystallise with the same symmetry, the full symmetry of the monoclinic system, are not truly isomorphous, as will be shown later. The compound (8) crystallises in the orthorhombic system with holohedral symmetry.

It is surprising to find that the *cis*-ammonium and *cis*-potassium compounds, (3) and (5), are isomorphous with the *cis*-barium compound (7), the former being salts of a univalent metal or radicle and the latter of a bivalent metal and therefore possessing a great difference in molecular weight and structure. Moreover, the compounds crystallise with a different number of molecules of water, the barium compound with three and the ammonium and potassium with one only.

*Potassium Ferri-oxalate*,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$  (Figs. 1 and 2).

A complete crystallographic examination of this substance has been made by Jaeger (*Rec. trav. chim.*, 1919, **38**, 242) and others. The results given below agree sufficiently well with those of Jaeger. He gives the symmetry as monoclinic holohedral, the axial angle  $\beta = 94^\circ 20'$ , and the axial ratio  $a : b : c = 0.9923 : 1 : 0.3925$ . The forms observed by him are the same as those given below. The measurements are recorded now for the sake of comparison with the isomorphous aluminium salt. A detailed determination of the optical characters has not previously been made.

*Crystal system*: monoclinic. Class: holohedral. Axial angle:  $\beta = 94^\circ 13\frac{1}{2}'$ . Axial ratio:  $a : b : c = 0.9916 : 1 : 0.3895$ .

*Forms observed*:  $B = \{010\}$ , well developed, elongated parallel to the zone  $[010, 11\bar{1}]$ ;  $m = \{110\}$ , small bright faces;  $o = \{111\}$ , small bright faces;  $c = \{\bar{1}11\}$ , large faces, striated and elongated parallel to the axis of the zone  $[010, 11\bar{1}]$ ;  $s = \{101\}$ , when present, much striated and elongated parallel to the zone  $[010, 11\bar{1}]$ .

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$Bm = (010) : (110)$	21	$45^\circ 8' - 45^\circ 28\frac{1}{2}'$	$45^\circ 19'$	*
$Bo = (010) : (111)$	19	$70^\circ 25' - 70^\circ 46'$	$70^\circ 34'$	*
$Be = (010) : (\bar{1}11)$	8	$69^\circ 29\frac{1}{2}' - 69^\circ 46'$	$69^\circ 39'$	$69^\circ 38\frac{1}{2}'$
$mo = (110) : (111)$	19	$58^\circ 38\frac{1}{2}' - 58^\circ 57'$	$58^\circ 48\frac{1}{2}'$	*
$oc = (111) : (\bar{1}11)$	19	$57^\circ 37\frac{1}{2}' - 58^\circ 58'$	$57^\circ 45\frac{1}{2}'$	$57^\circ 48\frac{1}{2}'$

*Habit*: the crystals are transparent, green in colour, and well developed. They can easily be obtained fairly large or small as desired. A common habit of the crystals is that of thin plates parallel to  $B = \{010\}$ . More usually, the habit is that shown in Fig. 1.

It might appear, at first sight, that a more natural mode of treatment would be to regard the faces of the forms  $\{\bar{1}11\}$  and

$\{101\}$  as prisms of the form  $\{210\}$  and pinacoids of the form  $\{100\}$ , respectively. The treatment adopted brings out, however, the strong pseudotetragonal symmetry which the crystals evidently possess, and also shows the marked similarity which exists between

FIG. 1.

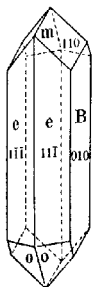


FIG. 2.

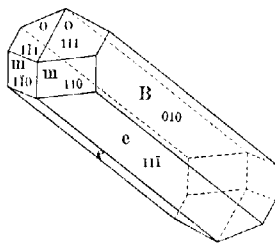


FIG. 3.

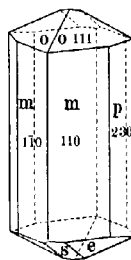


FIG. 4.

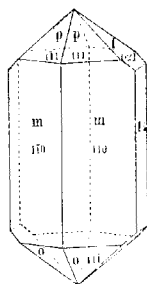


FIG. 5.

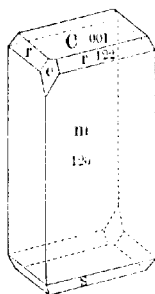


FIG. 7.

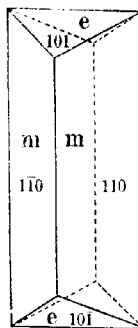
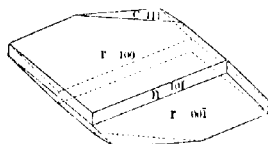


FIG. 6.



their angles and those of the crystals of the isomorphous aluminium compound. Fig. 2 shows a crystal drawn in the conventional position with the  $c$ -axis vertical.

*Cleavage*: none observed. A distinct parting parallel to  $\{111\}$  was observed.

*Density*: determined by suspension in liquid,  $d_4^{20} = 2.133$  (corrected).

*Topic axes*:  $\chi : \psi : \omega = 8.354 : 8.424 : 3.199$ .

*Optical characters*: refractive indices, measured by total reflection from  $B = (010)$ ,  $\alpha = 1.5019$ ,  $\beta = 1.5558$ ,  $\gamma = 1.5960$  for sodium light. The double refraction is therefore strong and the sign negative. The plane of the optic axes is  $B$ , and the acute bisectrix is inclined to the vertical axis,  $c$ , at an angle of about  $2^\circ$  in the obtuse axial angle. The optic axial angles in a liquid of refractive index about that of  $\beta$  were determined for lithium, sodium, and thallium lights and found to be as follows: Li,  $79^\circ 36'$ ; Na,  $78^\circ 49\frac{1}{2}'$ ; Tl,  $77^\circ 53\frac{1}{2}'$ . The dispersion shows  $\rho > \nu$ . Marked inclined dispersion of the bisectrices was also observed.

The pleochroism is fairly strong, the colour changing from dark green to very pale green. On looking through a crystal perpendicular to  $B = (010)$ , maximum absorption of light for vibrations perpendicular to the acute bisectrix and minimum absorption for vibrations parallel to that bisectrix were found.

*Potassium Aluminium-oxalate*,  $[\text{Al}(\text{C}_2\text{O}_4)_3]\text{K}_3 + 3\text{H}_2\text{O}$  (Fig. 3).

*Crystal system*: monoclinic. Class: holohedral. Axial angle:  $\beta = 93^\circ 23'$ . Axial ratio:  $a : b : c = 1.0061 : 1 : 0.3963$ .

*Forms observed*:  $B = \{010\}$ , present occasionally and then as very narrow faces;  $m = \{110\}$ , and  $p = \{230\}$ , well developed but much striated;  $o = \{111\}$ , and  $e = \{\bar{1}11\}$ , small, fairly good faces;  $s = \{\bar{1}01\}$ , small, narrow faces.

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$mm = (110) : (\bar{1}10)$	3	$89^\circ 40\frac{1}{2}' - 89^\circ 50'$	$89^\circ 46'$	*
$mp = (110) : (230)$	6	$11^\circ 1' - 11^\circ 14'$	$11^\circ 7'$	$11^\circ 18'$
$oo = (111) : (111)$	5	$39^\circ 29\frac{1}{2}' - 39^\circ 51'$	$39^\circ 37'$	$39^\circ 42'$
$es = (\bar{1}11) : (\bar{1}01)$	7	$20^\circ 17\frac{1}{2}' - 20^\circ 55'$	$20^\circ 35\frac{1}{2}'$	*
$mo = (110) : (111)$	8	$58^\circ 44\frac{1}{2}' - 59^\circ 17'$	$59^\circ 0\frac{1}{2}'$	$59^\circ 1'$
$oe = (111) : (\bar{1}11)$	4	$58^\circ 6' - 58^\circ 31'$	$58^\circ 19'$	$58^\circ 20'$
$em = (\bar{1}11) : (\bar{1}10)$	5	$62^\circ 40' - 63^\circ 0\frac{1}{2}'$	$62^\circ 50'$	*

*Habit*: the crystals were fairly large but poorly developed. They were colourless and more or less transparent. Their development was prismatic with either end terminated by four small pyramidal faces and one small dome.

*Cleavage*: none observed, but a well-marked although rough parting parallel to  $\{101\}$  was observed.

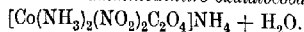
*Density*: determined by suspension in liquid,  $d_4^{20} = 2.026$  (corrected).

*Topic axes*:  $\chi : \psi : \omega = 8.300 : 8.442 : 3.273$ .

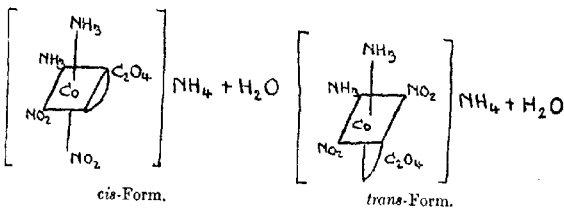
*Optical characters*: refractive indices as found by the immersion method,  $\alpha = 1.49$ ,  $\gamma = 1.50$ . The double refraction is weak and the sign positive.

The plane of the optic axes is  $B$ , and the acute bisectrix is inclined to the  $a$  axis at an angle of about  $11^\circ$  in the obtuse axial angle. The optic axial angles in benzene ( $\mu = 1.50$ ) were determined for lithium, sodium, and thallium lights and found to be as follows: Li,  $70^\circ 44'$ ; Na,  $71^\circ 12'$ ; Tl,  $71^\circ 35\frac{1}{2}'$ . The dispersion is apparently  $v > p$ . Marked inclined dispersion of the bisectrices was also observed.

*Ammonium Diamminodinitro-oxalatocobaltate*,



Two isomeric forms of this composition occur, one crystallising in the rhombohedral system and one in the monoclinic. They correspond with the following structural formulæ:—



*Ammonium cis-Diamminodinitro-oxalatocobaltate* +  $1\text{H}_2\text{O}$ .—  
*Crystal system*: rhombohedral. *Class*: ditrigonal scalenohedral.  
*Millerian axial angle*:  $\alpha = 107^\circ 57'$ . Angle over the edges of the primary rhombohedron,  $63^\circ 33'$ .

*Forms observed*:  $r = \{100\}$ , well developed;  $n = \{10\bar{1}\}$ , small, narrow faces;  $l = \{11\bar{1}\}$ , small, square faces.

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$rl = (100) : (11\bar{1})$	6	$85^\circ 35\frac{1}{2}' - 85^\circ 55'$	$85^\circ 43'$	$85^\circ 41'$
$nl = (10\bar{1}) : (11\bar{1})$	27	$43^\circ 3' - 43^\circ 54\frac{1}{2}'$	$43^\circ 29'$	$43^\circ 31'$
$rl = (11\bar{1}) : (100)$	31	$46^\circ 9' - 46^\circ 54\frac{1}{2}'$	$46^\circ 29'$	*
$nr = (10\bar{1}) : (100)$	35	$57^\circ 48\frac{1}{2}' - 58^\circ 47\frac{1}{2}'$	$58^\circ 16'$	$58^\circ 13\frac{1}{2}'$

*Habit*: rhombohedral. The crystals were very small but well-developed. They were deep reddish-brown in colour and so opaque as to preclude any determination of optical characters. The crystals are similar in appearance to those of the isomorphous barium compound (Fig. 6) with the difference that in this case basal planes are absent.

*Cleavage* : none observed.

*Density* : measured by suspension in liquid,  $d_4^{20} = 1.971$  (corr.).

*Topic axes* :  $\chi = \psi = \omega = 5.784$ .

*Ammonium trans-Diamminodinitro-oxalatocobaltate* +  $\text{H}_2\text{O}$  (Fig. 4).—*Crystal system* : monoclinic. Class : holohedral. Axial angle :  $\beta = 92^\circ 51\frac{1}{2}'$ . Axial ratio :  $a : b : c = 0.4089 : 1 : 0.3654$ .

*Forms observed* :  $B = \{010\}$ , occasionally present as long, narrow faces;  $m = \{110\}$ , fairly good, long, narrow faces;  $l = \{021\}$ ,  $p = \{111\}$ ,  $o = \{\bar{1}11\}$ , all very small faces.

*Angles measured* :

	No. of measure- ments.	Limits.		Mean. Obs.	Calc.
$mm = (110) : (\bar{1}\bar{1}0)$	5	48° 8'	—48° 16'	48° 12'	*
$Bp = (010) : (111)$	3	73 52½	—74 3	73 56½	*
$Bo = (010) : (\bar{1}\bar{1}1)$	2	72 48½	—73 3½	72 56	73° 21½'
$mp = (110) : (111)$	4	44 46	—44 52	44 48½	*
$po = (111) : (\bar{1}\bar{1}1)$	5	87 25½	—87 37½	87 32	87 45½
$Bl = (010) : (021)$	6	51 38	—52 13½	51 54	51 50½
$pl = (111) : (021)$	3	41 27½	—41 36½	41 32	41 25½
$lm = (021) : (\bar{1}10)$	4	77 2½	—77 22	77 12	77 31
$ol = (\bar{1}11) : (021)$	6	42 22½	—42 46½	42 33	42 42
$lm = (021) : (110)$	8	73 2½	—73 54	73 36	73 15½

*Habit* : prismatic, terminated by extremely small dome and pyramid faces. The crystals were very poorly developed. Hence it was not possible to obtain more than approximate measurements of the crystallographic angles. A strong pseudorhombic symmetry is shown, the axial angle differing from a right angle by less than  $3^\circ$  and the angles from  $B = \{010\}$  on to  $p\{111\}$  and  $o = \{\bar{1}11\}$  differing respectively by less than  $1^\circ$ . The larger crystals were hollow right through the centre, rendering them useless for optical study, and it was not found possible to make a complete determination of optical properties with the extremely small crystals which were not hollow.

*Cleavage* : none observed.

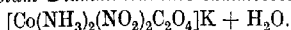
*Density* : measured by suspension in liquid,  $d_4^{20} = 1.879$  (corr.).

*Topic axes* :  $\chi : \psi : \omega = 4.224 : 10.33 : 3.775$ .

*Optical characters* : refractive indices as found by the immersion method, greater than 1.74 for vibrations parallel to the  $x$  and  $z$  axes and somewhat lower for those parallel to the  $y$  axis.

*Pleochroism* : colour changes from dark reddish-brown to light yellowish-brown, with maximum absorption of light for vibrations parallel to the  $x$  axis, minimum absorption for vibrations parallel to the  $z$  axis, and intermediate absorption for vibrations parallel to the  $y$  axis.

Nearly straight extinction parallel to the crystallographic axis  $c$  was observed.

*Potassium Diamminodinitro-oxalatocobaltiate*,

As in the case of the isomorphous ammonium salt, two isomeric forms of this composition occur, the *cis*-form, as before, crystallising in the rhombohedral, and the *trans*-form in the monoclinic, system.

*Potassium cis-Diamminodinitro-oxalatocobaltiate* +  $1\text{H}_2\text{O}$ .—*Crystal system*: rhombohedral. *Class*: ditrigonal scalenohedral. Millerian axial angle:  $\alpha = 107^\circ 54'$ . Angle over the edges of the primary rhombohedron,  $63^\circ 40'$ .

*Forms observed*:  $r = \{100\}$ , well developed;  $n = \{101\}$ , small, narrow faces;  $l = \{111\}$ , small, square faces;  $C = \{111\}$ , small, triangular faces, which occur only rarely and are very poor when present.

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$C: (111):(100)$	2	$37^\circ 24' - 37^\circ 44\frac{1}{2}'$	$37^\circ 34'$	$37^\circ 31'$
$rl = (100):(111)$	3	$85^\circ 32' - 85^\circ 44\frac{1}{2}'$	$85^\circ 39'$	$85^\circ 34\frac{1}{2}'$
$nl = (101):(111)$	8	$43^\circ 28\frac{1}{2}' - 43^\circ 41\frac{1}{2}'$	$43^\circ 34'$	$43^\circ 28\frac{1}{2}'$
$lr = (111):(100)$	20	$46^\circ 11\frac{1}{2}' - 46^\circ 55\frac{1}{2}'$	$46^\circ 31\frac{1}{2}'$	*
$nr = (101):(100)$	8	$58^\circ 1' - 58^\circ 21\frac{1}{2}'$	$58^\circ 12\frac{1}{2}'$	$58^\circ 10'$

*Habit*: rhombohedral with basal terminations rare. The crystals were extremely small but fairly well-developed. They were dark reddish-brown and too opaque to allow of the determination of optical properties. They were similar in appearance to the crystals of the isomorphous barium compound (Fig. 6).

*Cleavage*: none observed.

*Density*: determined by suspension in liquid,  $d_4^{20} = 2.007$  (corrected).

*Topic axes*:  $\chi = \psi = \omega = 5.874$ .

*Potassium trans-Diamminodinitro-oxalatocobaltiate* +  $1\text{H}_2\text{O}$  (Fig. 5).—*Crystal system*: monoclinic. *Class*: holohedral. Axial angle:  $\beta = 92^\circ 47\frac{1}{2}'$ . Axial ratio:  $a:b:c = 1.1558:1:0.9388$ .

*Forms observed*:  $A = \{100\}$ , very narrow faces, not always present;  $C = \{001\}$ , fairly good, lozenge-shaped faces, always present and the largest of the faces terminating the prisms;  $m = \{120\}$ , fairly well-developed, long faces, often striated perpendicularly to the prism edge;  $e = \{101\}$ , extremely small, generally triangular faces;  $r = \{122\}$ , very narrow faces;  $s = \{121\}$ , similar in development to the form  $r$ ;  $t = \{101\}$ , similar in development to the form  $e$ , but only once found.

In addition to these forms, the crystals from one crystallisation also showed faces which evidently belonged to the forms  $o = \{121\}$  and  $p = \{122\}$ , but as these crystals were extremely poor it was

not possible to obtain sufficiently accurate measurements of the angles from these faces on to *C* or *m* to establish their identity beyond doubt.

*Angles measured:*

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
<i>Am</i> = (100) : (120)	8	66° 14½' — 66° 52'	66° 35'	*
<i>Ac</i> = (100) : (101)	2	49 34½ — 49 48½	49 41½	49° 14½'
<i>eC</i> = (101) : (001)	3	37 56 — 38 0½	37 58	*
<i>Ct</i> = (001) : (101)	1		41 10½	40 11
<i>Cm</i> = (001) : (120)	4	88 40½ — 89 6½	88 53½	*
<i>Cr</i> = (001) : (122)	4	44 28 — 45 16	44 52	45 3
<i>ms</i> = (120) : (121)	5	25 27 — 26 32½	26 8½	26 17
<i>sC</i> = (121) : (001)	6	63 6 — 65 48½	64 45½	64 40½
<i>me</i> = (120) : (101)	5	74 35½ — 75 24	75 1½	74 58
<i>mr</i> = (120) : (122)	5	61 20½ — 62 36	61 59½	61 55

*Habit:* the crystals were extremely small and not well developed and only permitted approximate determinations of the crystallographic angles. They were prismatic with a prominent basal termination and with a certain number of very small pyramidal and domal faces.

*Cleavage:* none observed.

*Density:* measured by suspension in liquid,  $d_4^{20} = 2.093$  (corrected).

*Topic axes:*  $\chi : \psi : \omega = 6.080 : 5.260 : 5.043$ .

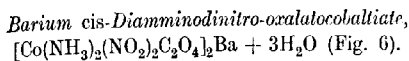
*Optical characters:* refractive indices as found by the immersion method,  $\alpha = 1.56$ ,  $\beta = 1.65$ ,  $\gamma > 1.74 < 1.77$ . The double refraction is therefore strong and the sign positive.

The optic axes lie in the plane of symmetry and the obtuse bisectrix is very slightly inclined to the crystallographic axis *c*. Hence the extinction is nearly straight. The optic axial angle is large.

*Pleochroism:* the colour changes from deep reddish-brown to yellowish-brown. Maximum absorption of light takes place for vibrations parallel to the *x* axis, minimum absorption for vibrations parallel to the *z* axis, and intermediate absorption for vibrations parallel to the *y* axis.

A comparison between the values of the angles obtained for this compound and for the *trans*-ammonium compound indicates a close relationship between them. The two compounds are, however, not truly isomorphous, for there is a complete difference of orientation between them, the plane of symmetry and the diad axis in the ammonium compound being at right angles to the respective positions they should occupy if it were isomorphous with the potassium compound. In both compounds a strong pseudo-c. hombic symmetry is evident. Had orthorhombic

symmetry been attained, the crystals of the two compounds would have shown true isomorphism.



*Crystal system*: rhombohedral. *Class*: ditrigonal-scalenohedral. Millerian axial angle  $\alpha = 108^\circ 16'$ ; angle over the edges of the primary rhombohedron,  $63^\circ 6'$ .

*Forms observed*:  $C = \{111\}$ , small, triangular faces, always present and fairly good;  $r = \{100\}$ , large, well-developed faces;  $n = \{10\bar{1}\}$ , very narrow and rather poor faces;  $l = \{11\bar{1}\}$ , extremely small faces, very rarely present.

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$Cr = (111) : (100)$	14	$36^\circ 43\frac{1}{2}' - 37^\circ 24\frac{1}{2}'$	$37^\circ 2'$	*
$rl = (100) : (1\bar{1}1)$	1		$86^\circ 35\frac{1}{2}'$	$86^\circ 30'$
$nr = (10\bar{1}) : (100)$	21	$57^\circ 56\frac{1}{2}' - 59^\circ 8\frac{1}{2}'$	$58^\circ 32'$	$58^\circ 27'$

*Habit*: rhombohedral with basal terminations. The crystals were extremely small and rather opaque and of a deep reddish-brown colour.

*Cleavage*: none observed.

*Density*: determined by suspension in liquid,  $d_4^{20} = 2.142$  (corrected).

*Topic axes*:  $\chi = \psi = \omega = 7.544$ .

*Optical characters*: refractive indices, measured by total reflection from  $\{111\}$ ,  $\epsilon = 1.5007$ .  $\omega$  is very high and could not be measured. The double refraction is strong and the sign is negative. On looking through some of the clearer crystals, perpendicular to the basal plane, in strong sodium light, a faint uniaxial interference figure was observed in convergent polarised light.

Table for the comparison of the *cis*-rhombohedral compounds.

Chemical composition.	Millerian axial angle.	Angle over edges of primary rhombo- hedron.	Molecular weight = $M$ .	Density, $d_4^{20}$ .	Topic axes, $\chi = \psi = \omega$ .	
					(1) Calculated using $M$ .	(2) Calculated using $2M$ .
$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_2\text{NH}_4 + \text{H}_2\text{O}$	$107^\circ 57'$	$63^\circ 33'$	309.11	1.971	5.784	7.288
$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_2\text{K} + \text{H}_2\text{O}$	$107^\circ 54'$	$63^\circ 40'$	330.17	2.007	5.874	7.401
$[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_2\text{Ba} + 3\text{H}_2\text{O}$	$108^\circ 16'$	$63^\circ 6'$	739.33	2.142	7.544	

A comparison of the crystallographic angles of the three rhombohedral *cis*-compounds makes evident their isomorphous relationship. This is a close one for all three compounds and in the case of the ammonium and potassium compounds is of an extreme closeness. The latter might be expected, since in such heavy



molecules the ammonium group and the potassium atom are a comparatively small part and therefore their substitution for one another would naturally have a very small effect on their crystallography. But, as pointed out early in this paper, the close isomorphism of the barium compound is not what would naturally be expected. No doubt, the reason given above for the extremely close isomorphism of the ammonium and potassium compounds applies in this case, but it does not seem sufficient to be the whole explanation. It may be that each barium atom takes the place of two ammonium groups or two potassium atoms in the crystal structure without greatly altering that structure. In this connection, it is interesting to note that if the topic axes for the ammonium and potassium compounds are calculated, using double their molecular weights, the values obtained are fairly close to that of the barium compound in which the single molecular weight is used. It would seem, however, that only an exact knowledge of the arrangement of the atoms in the crystal structure could afford a complete explanation.

*Ammonium Diamminotetranitrocobaltate*,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$   
(Fig. 7).

*Crystal system*: orthorhombic. *Class*: holohedral. *Axial ratio*  
 $a : b : c = 0.8677 : 1 : 0.5110$ .

*Forms observed*:  $m = \{110\}$ , large faces;  $e = \{101\}$ , fairly large faces;  $q = \{011\}$ , very small faces, rarely present.

*Angles measured*:

	No. of measure- ments.	Limits.	Mean. Obs.	Calc.
$ee = \{101\} : \{101\}$	2	$60^\circ 58' - 61^\circ 0'$	$60^\circ 59'$	*
$me = \{110\} : \{101\}$	7	$67^\circ 5' - 67^\circ 47\frac{1}{2}'$	$67^\circ 28'$	*
$mm = \{110\} : \{110\}$	4	$81^\circ 16' - 82^\circ 58'$	$82^\circ 2\frac{1}{2}'$	$81^\circ 54'$

*Habit*: simple prismatic, terminated by a pair of macrodomes. The crystals were extremely small and poorly developed. The angular measurements obtained are therefore only approximate. Owing to the poor quality of the crystals, their optical study was not undertaken, but it was found that their refractive indices were high, lying between 1.78 and 1.74 for vibrations parallel to the  $c$  axis and about 1.73 for vibrations in a direction perpendicular to the  $c$  axis and parallel to either the  $a$  or the  $b$  axis. The crystals were of a deep reddish-brown colour.

*Cleavage*: none observed.

*Density*: determined by suspension in liquid,  $d_4^{20} = 1.973$  (corrected).

*Topic axes*:  $\chi : \psi : \omega = 6.042 : 6.963 : 3.558$ .

The help afforded by Mr. A. Hutchinson in directing this work has been very much appreciated. Grateful acknowledgment is also made of the assistance of a grant from the Department of Scientific and Industrial Research.

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CCXLIX.—*The Ignition of Gases. Part II. Ignition by a Heated Surface. Mixtures of Methane and Air.*

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*Relative Ignition Temperatures.*

THE exposure of various inflammable mixtures to heated surfaces of known temperature was one of the earliest methods by which it was sought to determine the "ignition-temperatures" or "ignition-points" of the mixtures, and the values so obtained by different observers are still often quoted, without qualification. Yet some qualification is necessary, for the results so obtained for a given mixture are dependent in a considerable degree on the experimental conditions—on the character of the heated surface, for example, and on the ratio its area bears to the volume of the mixture. So much so, that "ignition-points" determined by such a method as that of Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], 4, 280), who measured the temperature to which the walls of a porcelain vessel had to be heated in order that the mixture undergoing test should inflame when it was rapidly admitted to the vessel, can only be regarded as possessing relative value.

A definition of "ignition-temperature" (following Nernst's), which has received some acceptance, though it is recognised to be inadequate, is: The lowest temperature to which a mixture of combustible gas and air or oxygen must be raised in order that the chemical action between the gas and the oxygen (unaided by exterior influences) can become so rapid as to produce flame.

If a mixture of an inflammable gas, methane for example, and air is gradually raised in temperature (below its ignition-temperature) throughout its extent by some external source of heat, such as the heated walls of a containing vessel, the rate of combination between the methane and the oxygen gradually increases. Since this reaction is accompanied by an evolution of heat, the products of it, and, *ipso facto*, any unburnt mixture with which they mingle, are at a higher temperature than the external source of heat; and, inasmuch as an increase in temperature augments greatly

the rate of reaction, there is a tendency for this rate of reaction to go on increasing until the whole of the methane, or of the oxygen, in the mixture is consumed. If, however, the initial temperature imparted to the mixture by the heated walls of the vessel is sufficiently high, the rate of reaction, being initially rapid, will soon become so rapid as to produce "flame"; that is to say, the combination between oxygen and methane, instead of proceeding at a steadily increasing speed to a conclusion (consequent on the exhaustion of one or other of the combining gases), will be completed comparatively suddenly by the passage of flame through the mixture.

It is clear that, for a given mixture, the value for the ignition-temperature as defined is not identical with the temperature existing in the mixture at the moment when flame actually makes its appearance. On the contrary, there must be a pre-flame period during which the rate of reaction is rapidly increasing. It will be understood, also, that the duration of this pre-flame period will vary with the character of the mixture, dependent on the rate of change of reaction-rate with temperature. Except under adiabatic conditions, also, the duration of the pre-flame period will depend on the facilities that are provided for the transference of heat from the rapidly combining mixture to its surroundings.

Now, the definition of "ignition-temperature" implies that heat shall be supplied to the mixture adiabatically, and that a specific property of the mixture will be measured. Herein, such methods as that of Mallard and Le Chatelier fail; for, however quickly the mixture of which the ignition-temperature is required is passed into the heated vessel, the whole volume cannot be raised at once to the temperature of the walls of the vessel, but those portions that reach the walls earliest will become raised in temperature first. Apart from the fact that this unequal heating may cause the portion that ultimately ignites to be different in composition from the original mixture admitted to the vessel, there will be a loss of heat to, and through, the walls of the vessel. In order to cause the ignition of the mixture, the initial temperature of the walls of the vessel must, in fact, be so high that the rate at which heat is produced by the combustion of the "layer" of mixture adjacent to them is greater than the rate of loss of heat through them. For this reason, it is evident that when the source of heat is a solid surface the attainment by a mixture of a temperature that will render the reaction self-heating is dependent, not only on the chemical and physical characteristics of the mixture, but also on the character and extent of the solid surface.

The importance, when attempting to determine the true "igni-

tion-points" of gaseous mixtures, of eliminating as far as possible the effect of contact with heated surfaces, was first pointed out by Dixon and Coward (T., 1909, 95, 514), who devised a new method of experiment whereby streams of the inflammable gas and of the air (or oxygen) could be heated separately, *pari passu*, and then allowed to mingle at a little distance from the ends of the tubes in which they were heated. This was found greatly to reduce, although not entirely to eliminate, the effect of surface action. The chief defect of the method, from the point of view of the present research, lies in the fact that it does not enable one to measure the variations in ignition-temperature that occur when the proportions of combustible gas and air in the mixtures are varied. The gas and air mingled with one another fortuitously, and, presumably, the ignition-temperature recorded for a particular combustible gas was that of its (indeterminate) most readily-ignited mixture with air, or oxygen, at atmospheric pressure.

The main object of the present research was to determine which was the most readily-ignited mixture of methane and air at atmospheric pressure; and not necessarily its true ignition-temperature. Despite the objections to Mallard and Le Chatelier's method of experiment as means of measuring true "ignition-points," it was therefore decided to employ a similar method, in the belief that relative values for different mixtures could best be obtained thereby.

Details of the method used are given in the experimental portion of this paper; briefly, the mixtures, of known composition, were admitted rapidly to an evacuated cylindrical vessel of quartz, of 81 c.c. capacity, which was heated in an electric tube-furnace. The lowest temperature to which the walls of the vessel had to be heated in order that a given mixture should ignite when admitted to it was taken to be the "ignition-temperature" of that mixture relative to that of other mixtures admitted to the same vessel. The results, which for mixtures of the same composition were remarkably constant (within 1°), were as follow:

Methane, per cent. in air.	Relative ignition- temperature.	Methane, per cent. in air.	Relative ignition- temperature.
2.00	711°	8.00	701°
3.00	700	8.80	707
3.95	696	10.00	714
5.85	695	11.75	724
7.00	697	14.35	742

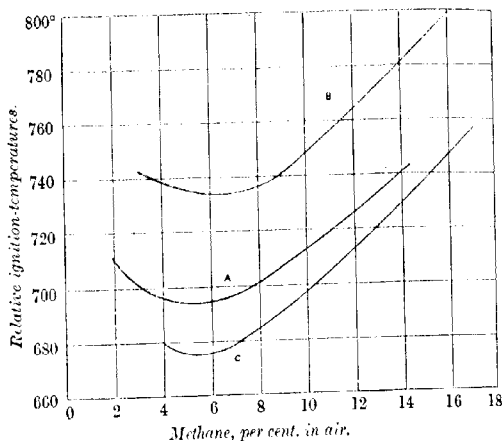
It will be noticed that the ignition of mixtures containing proportions of methane that are outside the limits of inflammability at atmospheric temperature is recorded; such mixtures can propagate flame at the much higher temperatures near their ignition-temperatures. Thus, when the mixture is at a temperature of

600°, the lower limit of inflammability of methane (downward propagation of flame) is 3.35 per cent. (see T., 1918, **113**, 45).

The results are shown graphically in Fig. 1 (curve A), similar results obtained by Taffanel and Le Floch (*Compt. rend.*, 1913, **157**, 469), who used quartz vessels of 15 c.c. (curve B) and 275 c.c. (curve C) capacity, being also shown. According to all three curves, the mixtures most readily ignited by a heated surface maintained in contact with them contain between 5 and 6 per cent. of methane.

The decrease observed in the "ignition-temperature" for a given mixture as the size of the heated vessel is increased can be explained

FIG. 1.

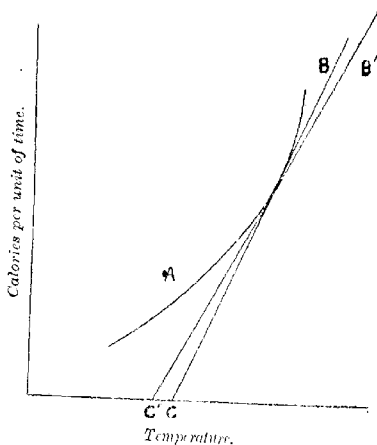


on the following considerations (see Le Chatelier, "Le Carbone," p. 261, Paris, 1908): If two curves, A and B (Fig. 2), are traced which represent, as a function of temperature, (A) the heat generated, in calories per unit of time, by the combustion of the mixture, and (B) the heat transmitted by the burning mixture to the walls of the vessel, A will show a rapid increase in the amount of heat generated, whilst B will be a straight line and will be tangential to A when the conditions are such that ignition of the mixture can just be effected; the point, C, at which it cuts the temperature axis being the "ignition-temperature" of the mixture under the conditions of experiment. The quantity of heat generated by the combustion of the mixture is proportional to its volume, although the rate of increase in the quantity with

temperature is not affected, so that the shape of curve *A* will not alter when the size of the heated vessel is increased. On the other hand, the rate at which the heat of the burning gases is transmitted to the walls of the vessel is proportional to the area of the walls, so that the inclination of curve *B* from the horizontal will vary with the ratio surface/volume of the vessel, being less as that ratio is less. For a larger vessel, therefore, a curve, *B'*, should be drawn, tangential to *A* and cutting the temperature axis at the lower "ignition-temperature," *C'*.

If the catalysing power possessed by the material of which the heated vessel is made is considerable (as it would be if a metallic

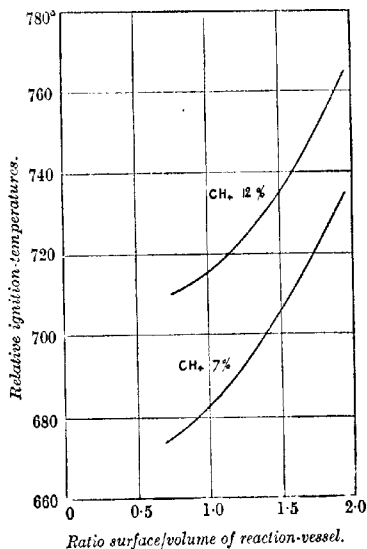
FIG. 2.



vessel was used), the fact that this power would be exercised in less degree the less the ratio surface/volume of the vessel would be an additional reason why the observed "ignition-temperature" of a given mixture should be lower the larger the vessel used. For, inasmuch as the catalytic action of the surface causes flameless combustion of the mixture to occur at temperatures considerably lower than its ignition-temperature, the production of flame is thereby delayed or even prevented. The mixture immediately surrounding the heated surface may be consumed so rapidly as to become incapable of propagating flame, the reaction continuing to take place only at or near the heated surface even although its temperature there may rise far above the true ignition-temperature of

the mixture. This effect of "surface-combustion" is illustrated by some experiments by Gautier and Helier (*Compt. rend.*, 1896, 122, 566) when using electrolytic gas ( $2\text{H}_2 + \text{O}_2$ ) as the inflammable mixture. On passing a stream of this mixture slowly through a heated tube packed with porous porcelain, no flame appeared until a temperature of  $840^\circ$  was attained; whereas for the same mixture Mallard and Le Chatelier found a temperature of  $550^\circ$  to be sufficient when using an unpacked tube.

FIG. 3.



A smooth quartz surface is a poor catalyst for the combustion of methane, and it is permissible to assume that the catalytic power per unit of area possessed by the material used by Taffanel and Le Floch for their reaction vessels was low and not very different from that of our vessel. We can then construct a curve, for any of the mixtures of methane and air, showing the variation in observed "ignition-temperature" with size of reaction-vessel, and thus gain some idea of the extent to which the observed values are departures from the true values. This has been done in Fig. 3 for mixtures containing 7.0 and 12.0 per cent. of methane, the relative ignition-temperatures being plotted against the ratios surface/volume for the three vessels, of 16, 81, and 275 c.c. capacity,

respectively. The curves are hyperbolic and, although extrapolation with a view to determine the true ignition-temperatures is inadmissible, we can judge how far the values recorded when the largest vessel was used are from those which would be obtained could the effects of surface combustion be eliminated and the conditions of heating be rendered adiabatic. As already stated, however, we are not primarily concerned, in this part of our research, with the determination of ignition-temperatures of mixtures of methane and air as physical constants; but we aim to record the relative ignitibilities of the different mixtures.

The mixtures of methane and air that are found to be most sensitive to ignition by a heated surface maintained in contact with them are those containing between 5 and 6 per cent. of methane; the most explosive mixtures (9.5 to 10.0 per cent. of methane) are decidedly more difficult to ignite by a source of heat of this character. Before considering this result further, it is desirable to examine another method whereby the sensitiveness of the mixtures to ignition by a heated surface can be measured, namely, the determination of the duration of the pre-flame period.

#### *The Pre-flame Period.*

We have already explained that the appearance of flame in a mixture cannot synchronise with the attainment of its ignition-temperature; there must always be an interval of time during which the self-heating of the mixture, which ultimately results in flame, is taking place. This interval may be so short (as with mixtures of hydrogen and oxygen) as to be barely measurable; or, as with mixtures of methane and air, it may be so long as to be readily noticeable.

Mallard and Le Chatelier (*loc. cit.*) first commented on the fact, which they thought to be peculiar to methane, that a mixture does not inflame as soon as it attains its "ignition-temperature," as represented by the temperature of the heated walls of a vessel to which it is admitted; and that mixtures of methane and air can, in fact, be maintained during several seconds at temperatures considerably higher than their ignition-temperatures without inflaming. This "retard à l'inflammation" they found to be as great as ten seconds for mixtures of methane and air in a vessel heated at a temperature of 650°. The "lag on ignition" diminished as the temperature of the vessel was increased and became inappreciable at 1000°.

The subject was studied more closely by Taffanel and Le Floch (*Compt. rend.*, 1913, 156, 1544), who made careful measurements of the "lags" for different mixtures of methane and air, using as



the means of ignition a quartz bulb of 300 c.c. capacity heated at temperatures of 700°, 800°, 900°, and 1000°, as follows :

<i>Lag on Ignition. Seconds. (Taffanel and Le Floch.)</i>				
Temperature .....	700°	800°	900°	1000°
Methane in air, per cent.				
6.5	1.35	0.72	0.19	nil
8.0	0.92	0.68	0.24	nil
10.0	—	1.12	0.33	0.14
12.0	—	1.73	0.30	nil

The explanation of the "retard à l'inflammation" advanced by Mallard and Le Chatelier was that the rate of reaction with mixtures of methane and air when dry was too slow, and that a certain amount of water vapour had to be formed by slow combustion before the rate could acquire the requisite speed; an explanation founded on Dixon's observations regarding the influence of moisture on the ignition of carbon monoxide by an electric spark. Taffanel and Le Floch have shown this analogy to be incorrect; nevertheless, the magnitude of the "lag" with the paraffins (it is greater still with the higher members of the series) can be ascribed to their protracted mode of combustion, and exemplifies the fact that the duration of the pre-flame period depends essentially on the rate of change of reaction-rate with temperature.

According to our experiments, the lag on ignition, with a number of mixtures containing between 2.5 and 13.0 per cent. of methane, lasted between ten and fifteen seconds when the heated vessel was just at the "relative ignition-temperature" for each mixture. With the vessel at higher temperatures, the lags were of shorter duration; they were constant for a given mixture and could be measured with considerable accuracy. The results can be conveniently shown graphically, as in Fig. 4, in which, for several different temperatures of the reaction-vessel, percentages of methane are plotted against their lags on ignition (in seconds).\*

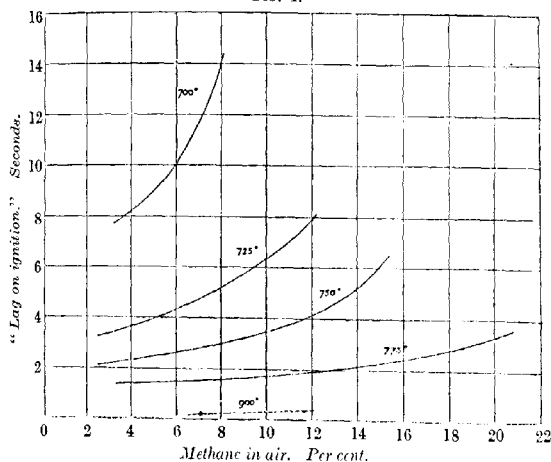
The more ready ignitibility of mixtures containing an excess of oxygen is emphasised by these experiments. In each series, the source of heat was at a higher temperature than the ignition-temperature of any of the mixtures, and it will be seen that, in each instance, the lag on ignition was of shortest duration with the mixture containing the lowest percentage of methane. A source of heat of given intensity, of the same character as that

\* A curve representing the experiments of Taffanel and Le Floch at 900° is included in Fig. 4; when comparing this curve with ours, it must be remembered that the reaction-vessel used by Taffanel and Le Floch was of larger capacity (300 c.c. as compared with 81 c.c.) than ours.

employed in the experiments, would have to remain in contact longer with, say, a 10 per cent. mixture of methane and air than with one containing 6 per cent. in order to ignite it.

As the temperature of the source of heat was increased beyond the "relative ignition-temperature" of a given mixture, the duration of the lag rapidly decreased (see Fig. 5), and it may be assumed that at temperatures of about  $1200^{\circ}$  the ignition of any of the mixtures would be nearly instantaneous; how nearly instantaneous it is of importance to determine (as regards the ignition of mixtures of firedamp and air in coal mines) and research on this subject, which requires more refined methods of time-measurement

FIG. 4.

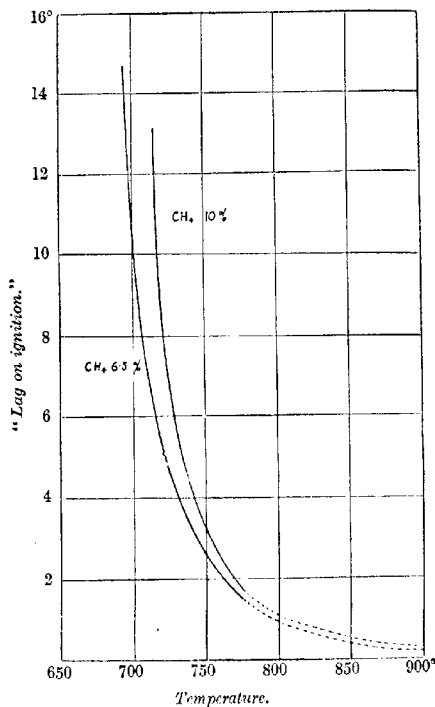


than those used for the work described in this paper, is in progress. From the slope of the curves in Fig. 4 it can be judged that, when the heated surface is at a temperature so much above the ignition-temperatures of the mixtures as  $1200^{\circ}$ , differences in the duration of the lags as between one mixture and another almost disappear, and that, to differentiate between the "ignitibilities" of the mixtures when exposed to such a source of heat, very small intervals of time have to be measured.

Judged by two standards, mixtures of methane and air containing an excess of oxygen are the most readily ignited by a heated surface. This is most clearly shown by the measurements of the time taken for flame to appear when the mixtures were exposed to a surface heated at a higher temperature than their

ignition-temperatures (Fig. 4); and it is shown also by their relative \*ignition-temperatures (Fig. 1). The natural inference is that, at a given temperature, the rate of reaction between methane and oxygen increases with the oxygen concentration. This we have actually found to be so, in experiments in which different mixtures of methane and air were slowly circulated over a porcelain surface

FIG. 5.



heated at 450°; but the explanation is still to seek. The tentative suggestion by Dixon and Crofts, to account for similar results obtained with mixtures of hydrogen and oxygen (T., 1914, 105, 2027), that the oxygen is "activated," does not cover all the known facts; unless one assumes that oxygen is thus "activated" only when in the presence of certain inflammable gases and not in the presence of all. If this is so, we still require to know why it is that some gases have this effect and others have not.

Turning now to a consideration of the igniting power of the source of heat, as distinct from the ignitibility of the mixture, it is obvious that this is dependent on the conditions under which it is presented to the mixture to be ignited. We have shown that, under certain experimental conditions, a quartz surface heated at a temperature of  $775^{\circ}$  would not ignite any mixture of methane and air if it was allowed to remain in contact with the mixture during only one second. What, then, would be the igniting power—the incendivity—of such a surface, maintained at such a temperature, were the mixtures to flow past or circulate around it? It would then seem probable that, inasmuch as the time of contact between any given portion of the mixture and the surface might well be less than one second, because of the continuous renewal of the mixture by the moving current, it could not cause ignition. Such was the experience of Mallard and Le Chatelier in their earliest attempts to determine ignition-temperatures by causing the mixtures to flow through heated tubes; a higher temperature was required for the heated surface to ignite a current of a given mixture flowing through the tube, an observation confirmed by Meyer and Freyer (*Ber.*, 1892, 25, 622).

In order to ignite a given mixture, the source of heat (the heated walls of the quartz vessel in the present instance), besides being of sufficient temperature, must be maintained in contact with the mixture during the period of acceleration of the rate of reaction which ultimately results in the production of flame (that is, during the period of "lag"), otherwise the acceleration will be retarded. The incendivity of a heated surface depends, therefore, on (*a*) its temperature and (*b*) its duration, or its time of contact with the mixture. To these must be added (*c*) its catalysing power, which, by inducing flameless combustion, reduces the incendivity of the surface.

#### EXPERIMENTAL.

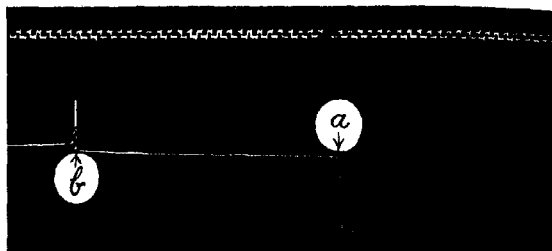
The apparatus consisted essentially of a transparent quartz bulb 8.5 cm. long and of 3.5 cm. internal diameter, connected by wide-bore tubing through mercury-seal taps with a gas-holder, and a recording pressure-gauge. The bulb, and some of the connecting tubing, lay within a platinum-wound, electric-resistance tube-furnace, the winding of which was so arranged that a uniform temperature, over the range  $500$ – $800^{\circ}$ , was obtained along that portion of the tube occupied by the quartz bulb, which fitted closely within the furnace. Temperatures were recorded by means of a platinum-iridium thermo-couple, lying between the bulb and the furnace tube.

The gas-holder contained the required mixture of methane and

air over a mixture of glycerol and water in equal parts by volume. Each mixture was analysed before use and was prepared from methane (of 99.8 per cent. purity), obtained by the liquefaction and fractional distillation of firedamp, and air, purified by passing through a dilute solution of potassium hydroxide. Connection could be made, through a three-way T-tap on the gas-holder, with a vacuum pump.

The pressure-gauge traced, on a smoked paper chart attached to a revolving drum, a continuous graph of the pressure within the quartz vessel, thus recording (*a*) (Fig. 6) the moment when the previously evacuated vessel was filled with the inflammable mixture at atmospheric pressure, and (*b*) the moment when a sudden rise in pressure, indicative of inflammation, occurred. The interval between (*a*) and (*b*) represented the "lag on ignition." Half-

FIG. 6.



seconds were recorded on the revolving chart by an electro-magnetic stylus.

When conducting an experiment to determine the "ignition-temperature" of a mixture, a constant temperature was obtained by regulating the electric current passing in the furnace, and was maintained during half-an-hour before a determination was made; two hours were allowed to elapse between successive determinations. The volume of gas required to fill the vessel at atmospheric pressure at the experimental temperature was calculated, and that volume (together with the small amount required to occupy dead space) was allowed quickly to enter the evacuated system from the gas-holder. If ignition occurred, flame could be observed through a window in the electric furnace, or the movement of the pressure gauge could be watched. The method of determination was that of "trial and error," and an accuracy within  $1^\circ$  is believed to have been obtained.

At the beginning of the investigation, some trouble was experienced, due, apparently, to a change in the catalysing power of the quartz surface, which manifested itself in particular if air was admitted to the heated vessel and allowed to remain (overnight, for example), and was noticeable also if the heated vessel remained evacuated for any length of time; the "ignition-temperature" of a given mixture tended to be lower after such treatment. This trouble was overcome by treating the surface after each determination with nitrogen, which was allowed to remain, at atmospheric pressure, within the heated vessel until it was required for the next determination. No change has been observed in the ignition-temperatures of a given mixture and air, as determined in this apparatus, during two years, and it can be assumed that the regular treatment of the surface with nitrogen has preserved constant its catalysing power.

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CCL.—*Physical Chemistry of the Oxides of Lead.*  
*Part VI. The Anodic Behaviour of Lead and*  
*Lead Dioxide.*

By SAMUEL GLASSTONE.

In a previous communication (this vol., p. 1469), the abnormal electromotive behaviour of electrolytic lead dioxide has been explained by assuming the presence in it of minute traces of a higher unstable oxide, possibly  $PbO_3$ . In order to obtain further evidence of the existence of such an oxide, a series of experiments, on the polarisation and discharge of lead and lead dioxide anodes in alkali, was carried out. Since the electrode potentials of the known oxides of lead in *N*-sodium hydroxide have already been determined, measurements of potential during polarisation and discharge should give information regarding the existence of any oxides in addition to those with which we are already familiar.

Elbs and Forssell (*Z. Elektrochem.*, 1902, **8**, 760) found that at low current densities a lead anode dissolves in *N*-sodium hydroxide as bivalent ions, but at higher densities the lead no longer dissolves, but lead dioxide is deposited, and oxygen is evolved. These authors attribute the evolution of gas to the decomposition of the dioxide into monoxide and oxygen, and state that this reaction occurs at a potential 0.23 volt more positive than that required for the deposition of lead dioxide from a solution of *N*-sodium hydroxide

saturated with lead monoxide. Observations and measurements to be described in the present paper, however, appear to show that oxygen evolution at a lead anode takes place through the intermediate formation of an unstable oxide, more highly oxygenated than the dioxide. Lorenz and Lauber (*Z. Elektrochem.*, 1909, **15**, 157) polarised lead plates anodically in sulphuric acid and followed the back *E.M.F.* by discharging through a high resistance. Fourteen different halts in the discharge potential were reported, eight of which were said to correspond with the electrode potentials of the oxides of lead measured by Streintz and Neumann (*Wied. Annalen*, 1890, **41**, 97). Lorenz and Lauber make no mention of an oxide higher than the dioxide, although it may be pointed out that a potential of 2.05 volts is attributed to the electrode  $\text{Pb}|\text{PbO}_2$  (which is actually  $\text{PbO}_2|\text{PbSO}_4$ , owing to the instability of the system lead-lead dioxide in sulphuric acid), and to the potential of the electrode  $\text{Pb}|\text{PbSO}_4$  is given the probably correct value of  $-0.29$  volt. From these figures, the ordinary lead accumulator should have an *E.M.F.* of 2.34 volts, which is, of course, much higher than the actual value. The second halt in the discharge potential was found to be 1.62 volts; this probably represents the reaction  $\text{Pb}^{+++} \rightarrow \text{Pb}^{++}$  (that is,  $\text{PbO}_2|\text{PbSO}_4$ ), for then the lead accumulator should have an *E.M.F.* of 1.91 volts, which is in close agreement with the actual value if the sulphuric acid is about 2*N*. It therefore appears that the potential of 2.05 volts is to be attributed to an oxide higher than the dioxide.

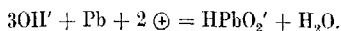
#### EXPERIMENTAL.

A simple cell was made up consisting of a platinum foil kathode, 6 sq. cm. in area, and an anode of either pure lead (series I and II) or lead dioxide (series III and IV). The anodic potential was measured during charge and discharge by comparison with a standard mercuric oxide half-element, the connecting tube of which was drawn out into a fine jet, which pressed close up against the anode.

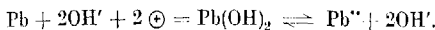
##### *Series I.*

The anode was a small sheet of lead connected with a platinum wire; the whole was completely waxed over, and an area of about 2 sq. cm. of the lead scraped clean and bright. A small pit was made in the surface, and the jet of the standard electrode fitted into it. The electrolyte used in this series was *N*-sodium hydroxide, and all measurements were made at room temperature (about 17°). The direct anodic potential (with current flowing) was measured from time to time, with different current densities. With low

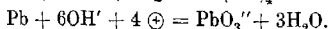
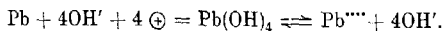
densities, up to 0.025 amp./cm.<sup>2</sup>, the anodic potential remained almost constant at -0.53 volt; lead dissolved at the anode, but there was no evolution of oxygen. At the kathode, however, lead was deposited and also hydrogen evolved, consequently more lead went into solution than was deposited. The potential of -0.53 volt corresponds with that of the half-element  $\text{Pb}|\text{PbO N-NaOH}$  (-0.56 volt), the small difference being probably due to concentration polarisation. The action at the anode is therefore the discharge of  $\text{OH}'$  ions, and the dissolution of lead as plumbite:



A certain amount of lead also went into solution as bivalent plumbous ions:



If the current density is increased further, for example, to 0.03 amp./cm.<sup>2</sup>, after a few minutes the current, as registered on an ammeter in the circuit, will suddenly decrease to about one-half of its previous value, and at the same time a dark grey film will be seen to creep across the hitherto clean surface of the lead anode. Coincident with this, the anodic potential suddenly rises to 0.70 volt, but there is still no evolution of oxygen. A much higher potential is now necessary to cause lead to dissolve, passivation being undoubtedly due to the visible coating of oxide. This is probably the dioxide, since neither lead sesquioxide nor red lead, both of which give plumbous ions in solution (see Part IV, this vol., p. 1456), would be likely to cause such a large increase of potential, namely, from -0.53 to 0.70 volt. The lead is apparently dissolving as plumbic and plumbate ions:



The presence of plumbate in the electrolyte may be readily shown by the addition of dilute nitric acid, when a precipitate of lead dioxide is formed.

After a few more minutes, a further, but smaller, decrease in the current occurs, and a black film now passes over the surface of the anode. At the same time, the anode potential rises to 1.18 volts, and when the dark film completely covers the anode, evolution of oxygen commences. This second film, which causes such a high anodic potential, is very probably a higher oxide; since evolution of oxygen takes place only after the formation of this film, it appears that gas formation is due to the continual form-



ation and decomposition of this higher oxide.\* Foerster (*Z. physikal. Chem.*, 1909, **69**, 236) and Grube (*Z. Elektrochem.*, 1910, **16**, 621) have similarly correlated the evolution of oxygen at a platinum anode with the formation of the oxide  $\text{PtO}_3$ , and possibly  $\text{PtO}_4$ . Similar conclusions have been drawn by Müller (*ibid.*, 1907, **13**, 133) and Foerster (*loc. cit.*) for the evolution of oxygen at copper, nickel, and iridium anodes.

If the current density is kept constant at 0.03 amp./cm.<sup>2</sup>, the anodic potential rises slowly to 1.26 volts, but no further changes occur.

Newbery (*T.*, 1916, **109**, 1066) measured the overvoltage at a lead anode in *N*-sodium hydroxide, using the commutator method; only one overvoltage condition is mentioned, namely, 0.6 to 1.0 volt (that is, an anodic potential of 1.0 to 1.4 volts) depending on the current density. These figures correspond with the third anodic potential of the present series of measurements.

*Discharge Potential.*—After three hours' polarisation at 0.03 amp./cm.<sup>2</sup>, the current was stopped, and the potential of the anode during self-discharge measured against that of a standard electrode. The initial fall from 1.26 to 0.82 volt occupied thirty-two seconds, and therefore very little of the high potential at the anode could have been due to the "transfer resistance" of oxide or gas film. During subsequent discharge, lasting twenty-one minutes, there was an indication of a break at 0.59 volt, a perfectly definite halt at 0.29 to 0.25 volt, and then a rapid drop to -0.56 volt. On allowing the electrode to stand, the potential rose again to 0.29 volt, at which value it remained for some time. The possible halt at 0.59 volt does not correspond with any known potential of the lead oxides, but the break at 0.29 to 0.25 volt was evidently due to mixtures, or more probably, solid solutions of lead monoxide, sesquioxide, and red lead, electromotively active with lead dioxide. After the discharge, a light brown coating of oxide had formed on the anode, and analysis showed it to contain lead monoxide and dioxide in the ratio of 1 : 0.85. This composition would agree with that of the mixture or solid solution suggested to account for the measured potential.

*Recharging of a Discharged Anode.*—The results obtained on recharging a discharged anode were substantially the same as

\* Since the completion of this work in April 1922, Grube (*Z. Elektrochem.*, 1922, **28**, 273) has reported the results of a set of experiments similar to those in series I. A number of the figures given are identical with those quoted above, but whereas Grube is apparently of the opinion that the potential of 0.79 volt is the beginning of a second stage which goes on gradually to about 1 volt, the present author, as a result of his observations, concludes that these two voltages represent two distinct stages of anodic reaction.

those obtained with a fresh anode. At small current densities, the lead was found to dissolve in the bivalent condition at an anodic potential of  $-0.53$  volt; with higher densities, the potential rose to  $0.7$  volt, and the oxide film was dark brown. It thus appears that lead coated with sesquioxide or red lead will still dissolve in the bivalent condition at low potential, consequently the film formed at  $0.70$  volt must be the dioxide. Unfortunately, it was not found possible to coat a lead surface with an oxide that could be definitely stated to be the dioxide, in order to confirm the view that the second stage of anodic potential is due to lead dioxide.

*Additional Experiments.*—By applying a fairly large current density, for example,  $0.05$  amp./cm.<sup>2</sup>, evolution of oxygen took place almost immediately at an anodic potential of  $1.20$  volts, rising to  $1.30$  volts; the intermediate stages were not observed. If the current density was now reduced, for example, to  $0.008$  amp./cm.<sup>2</sup>, the gas evolution was maintained at a potential of  $0.93$  volt. Further, if the polarising current was interrupted for some seconds, and then renewed at a low density, insufficient to cause evolution of oxygen at a fresh or discharged anode, gas evolution recommenced immediately. It appears that gas evolution takes place through the intermediate formation of an oxide, some of which would still be present on the anode even after the polarising current was stopped, rather than through a gas film only, which would have been rapidly destroyed on breaking the current.

### Series II.

The anode used was identical with the one employed in series I, but the electrolyte was *N*-sodium hydroxide saturated with lead monoxide. The three different stages of anodic potential were again observed, oxygen being evolved only when the potential had risen to  $0.9$ – $1.0$  volt. The latter stage was reached at a lower current density than in series I, probably owing to the fact that lead dioxide is readily deposited by the electrolysis of plumbite solutions, and therefore it would not be necessary to wait for the oxidation of the lead anode. The following potentials were obtained after ten minutes' polarisation at different current densities:

Current density (amp./cm. <sup>2</sup> )	0.006	0.017	0.03	0.09	0.135
Potential .....	0.90	0.92	0.98	1.00	1.11 volt

On the whole, the potentials are lower than those obtained in series I, corresponding with the fact noted in previous work (Part V, this vol., p. 1469) that the unstable higher oxide decomposes more readily in a solution of alkaline plumbite than in alkali alone.

During discharge a very rapid fall of potential to 0.7 or 0.5 volt occurred, depending on the initial potential before discharge. A definite decrease in the rate of fall occurred between 0.33 and 0.23 volt, after which the potential fell rapidly to -0.56 volt.

#### Series III A.

The anode used was a sheet of platinum foil, 3 sq. cm. in area, covered with electrolytic lead dioxide which had become stabilised as a result of keeping in a mixture of lead monoxide and *N*-sodium hydroxide (compare Part V). The electrolyte used was *N*-sodium hydroxide, and the anodic potentials obtained after ten minutes' polarisation at different current densities were :

Current density (amp./cm. <sup>2</sup> )	0.002	0.007	0.015	0.03	0.06	0.2
Potential .....	0.97	1.08	1.12	1.17	1.24	1.33 volt

In the case of very low current densities (for example, 0.002 amp./cm.<sup>2</sup>), the potential gradually rose from 0.72 volt to 0.94 volt, evolution of oxygen taking place only at the higher voltage. No other overvoltage stage was observed.

On allowing the anode to discharge after an hour's polarisation at a potential of 1.33 volts, the potential fell to 0.88 volt in thirty seconds, and therefore, as in series I, very little of the high potential could have been due to transfer resistance. From 0.78 volt, the rate of self-discharge was so small that the anode was discharged by short-circuiting with a Pb|PbO *N*-NaOH electrode of fairly large capacity. Halts were observed at 0.40 and 0.27 volt. On keeping in open circuit, the potential of the anode recovered to 0.29 volt; both these values and the colour of the anodic deposit suggested the presence of lead sesquioxide. During the initial self-discharge, evolution of oxygen was distinctly visible at the anode. It should be noted that in addition to the halts observed with a lead anode, there is also a break at 0.40 volt; as previously suggested (see Part V), this may be due to an oxide of platinum.

#### Series III B.

In this series, freshly deposited electrolytic lead dioxide on platinum was used as anode, the electrolyte being, as before, *N*-sodium hydroxide. The anodic potentials were slightly higher than in series III B for the same current densities :

Current density (amp./cm. <sup>2</sup> ) ...	0.002	0.015	0.2
Potential .....	1.09	1.18	1.36 volt

The higher potentials are probably due to the fact that the fresh electrolytic dioxide already contains some of the unstable oxide which is responsible for the high potentials. After one hour's

polarisation, the rate of self-discharge was so slow as to be inexplicable by any other means than that of the decomposition of an oxide. The potential at the time of interrupting the polarising current was 1.36 volts, and the subsequent potentials were :

Time (secs.) .....	12	55	105	150	260	270
Potential .....	1.02	0.92	0.88	0.866	0.852	0.842 volt

On allowing to discharge by short-circuiting with a Pb|PbO electrode, the usual halts at 0.40 and 0.30 volt were observed.

Using the so-called hydrated lead dioxide (Wernicke, *Pogg. Annalen*, 1870, **139**, 132) deposited on platinum, the results obtained during charge and discharge were quite similar to those obtained with lead dioxide deposited from lead nitrate solutions (compare Part V).

#### Series IV.

Series III *A* and *B* were repeated, using *N*-sodium hydroxide saturated with lead monoxide as electrolyte. The results obtained were almost identical with those obtained in series III, except that the rate of self-discharge was much greater, for example, from 1.30 to 0.84 volts in three seconds.

In series II and IV, where the electrolyte had contained sodium plumbite, a yellow precipitate formed round the anode during the passage of the polarising current. A specimen of this was washed and dried and found to contain monoxide and dioxide in the ratio of 1:0.63, and to lose 10.35 per cent. of its weight on heating. This analysis agrees well with that of a mixture of  $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{PbO} \cdot \frac{1}{2}\text{H}_2\text{O}$ . The plumbite solution has thus been anodically oxidised to plumbate, and the sesquioxide precipitated as a result of the plumbite-plumbate-hydroxyl equilibrium asserting itself (Part IV, *loc. cit.*). Grube (*Z. Elektrochem.*, 1922, **28**, 273) has recently observed the anodic oxidation of plumbite to plumbate; in concentrated alkali solution, the solid plumbate is precipitated. Becquerel (*Ann. Chim. Phys.*, 1843, [iii], **8**, 402), Beetz (*Pogg. Annalen*, 1844, **61**, 209), and Elbs and Forssell (*loc. cit.*) all noted the formation of this yellow precipitate during the direct electrolysis of plumbite solutions, but although the presence of lead dioxide in some form was observed, no mention was made of the sesquioxide. Jirsa (*Z. physikal. Chem.*, 1920, **94**, 1), using an alternating current of 49 periods, found that plumbite is oxidised to plumbate at various electrodes, and that lead sesquioxide is formed at palladium electrodes.

#### Conclusion.

Evolution of oxygen at a lead or lead dioxide anode takes place at almost identical potentials. In the latter case, the presence of

a higher oxide has been indicated by the slow fall of potential on self-discharge, whilst, in the former, the appearance of a black film, which is probably not the dioxide, corresponds with a sudden increase of anodic potential and to evolution of oxygen. From these two points of view, there seems very little doubt that evolution of oxygen at lead or lead dioxide anodes is due to the intermediate formation of an unstable higher oxide, which is probably present only in very small amounts in solid solution in the dioxide.

Féry (*J. Physique*, 1916, **6**, 21, 187) claimed to have proved that the activity of a lead accumulator is due to the presence of one or more higher oxides of lead. McInnes, Adler, and Joubert (*Trans. Amer. Electrochem. Soc.*, 1920, **37**, 641) examined the evidence and concluded that not only had Féry not proved that the activity of the accumulator is due to an oxide higher than the dioxide, but also he had not even shown that such an oxide exists. The present author has confirmed these conclusions, but is of opinion that the initial high *E.M.F.* of a lead accumulator obtained soon after charging may be due to an unstable higher oxide present only in extremely small amount.

The author's best thanks are due to Professor A. J. Allmand for his interest in this work.

UNIVERSITY COLLEGE, EXETER.

[Received, July 31st, 1922.]

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### CCLI.—*The Isomerism of the Oximes. Part X. Cinnam- and Nitrocinnam-aldoximes.*

By OSCAR LISLE BRADY and CLIFFORD DANE THOMAS.

PREVIOUS work (Brady and Dunn, *T.*, 1916, **109**, 650) has shown that Hantzsch's original method (Hantzsch and Miolati, *Z. physikal. Chem.*, 1892, **10**, 1; Hantzsch, *ibid.*, 1894, **13**, 509) for the determination of the configuration of the aldoximes is the only satisfactory one. This method consists in treating the oxime with warm, pure acetic anhydride and subsequently decomposing the excess of anhydride with sodium carbonate solution. In some cases, an acetyl derivative is formed, which, on hydrolysis with 2*N*-sodium hydroxide, regenerates the original oxime, whilst in others the corresponding nitrile is produced; occasionally, an acetyl compound is formed, which, however, is at once decomposed by 2*N*-sodium hydroxide, giving the nitrile (compare Wentworth and Brady, *T.*, 1920, **117**, 1045). To the first class of oximes is given the *anti*- and to the second the *syn*-configuration.

On this criterion, the aliphatic aldoximes differ from benzaldoxime and substituted benzaldoximes in that, as ordinarily prepared, they have the *syn*- as opposed to the *anti*-configuration; further, these *syn*-compounds, unlike the benz*syn*aldoximes, are stable and do not readily undergo isomeric change (compare Dollfus, *Ber.*, 1892, **25**, 1908). Particular interest attaches, therefore, to oximes of the type of cinnamaldoxime in which the oximino-group is at the end of a chain and a benzene ring is also present in the molecule. It would be expected that such compounds would approximate to the aliphatic type, but this has not been borne out by the results now obtained.

The oximes of cinnamaldehyde have been investigated by Bamberger and Goldschmidt (*Ber.*, 1894, **27**, 3429), who showed that by the action of hydroxylamine hydrochloride on the aldehyde in the presence of aqueous sodium hydroxide a mixture of the two oximes was produced. These were oriented by Hantzsch's method (see also Dollfus, *loc. cit.*), and it was shown also that the *anti*- could be converted into the *syn*-isomeride in the usual way through the hydrochloride. Beyond this, little has been done with this class of compound. The effect of substitution in the ring on the relative stability of the isomerides in the case of the benzaldoximes is so puzzling that the investigation of the substituted cinnamaldoximes has been undertaken. Contrary to expectation, it has been found that the oximes as usually prepared from *o*-, *m*-, and *p*-nitrocinnamaldehydes possess the *anti*-configuration, and so far it has not been possible to obtain the *syn*-derivatives in the usual way. Bamberger and Goldschmidt's method for the preparation of the mixture of cinnam*anti*- and cinnam*syn*-aldoximes gave a low-melting product from which it was difficult to obtain satisfactory yields of either isomeride in a pure condition, and various modifications of their process have been tried. Whilst it has been possible to devise a method giving fairly satisfactory yields of the *syn*-compound, no improvement has been effected in the preparation of the *anti*-derivative by direct oximation. In connexion with another investigation, the benzoyl derivative, obtained from cinnam*syn*aldoxime by Bornemann (*Ber.*, 1886, **19**, 1512) by the Schotten-Baumann reaction, was prepared. Bornemann's work was done before the isomerism of the aldoximes had been observed, but his derivative is described in Richter's "Lexicon" as benzoylcinnam*syn*aldoxime. When, however, this compound was hydrolysed with sodium hydroxide solution, it was found that, instead of cinnam*anti*nitrile, an oxime melting at 76° was produced. The *anti*-oxime extracted from the oximation product of cinnamaldehyde by Bamberger and Goldschmidt's method was found to melt rather indefinitely at 64–65° as stated by these authors, and it seemed at first as if a new

isomeride had been obtained. It was found, however, that the oxime melting at 76° gave the same acetyl derivative and the same benzyl and dinitrophenyl ethers as that melting at 64–65°, and that it was converted through the hydrochloride into the original cinnam. *syn*aldoxime. Further, a mixture of the two substances melted between 64° and 76°, according to the proportions taken. Investigation of the method of separation employed by Bamberger and Goldschmidt, namely, extraction with light petroleum, showed that the *syn*-compound was appreciably soluble in this solvent when hot, but very sparingly soluble when cold. Under these conditions, it is common experience that it is a matter of considerable difficulty to obtain the more soluble compound pure, and there seems no reason to doubt that Bamberger and Goldschmidt's *anti*-oxime was contaminated with the *syn*-derivative.

Cinnam. *syn*aldoxime is apparently quite stable under normal conditions. Unlike benz. *syn*aldoxime, it is not changed into the *anti*-isomeride by traces of hydrochloric acid, and its solution in 2*N*-sodium hydroxide, when heated on the water-bath for an hour or kept at room temperature for a week, undergoes no change, the *syn*-oxime being precipitated therefrom by carbon dioxide or by dilute acids. The conversion of a stable *syn*-oxime into the *anti*-isomeride in this way through the benzoyl derivative differs from all other cases of oxime isomeric change so far investigated, and promises interesting developments.

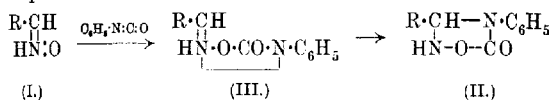
Although the *syn*-oxime is the main product of the oximation of cinnamaldehyde, when the aldehyde is acted on by  $\alpha$ -benzylhydroxylamine the *anti*-*O*-benzyl ether is almost exclusively formed; a very small quantity of a higher-melting product was obtained, insufficient, however, for further investigation.

The carbanilino-derivatives of cinnam. *anti*- and cinnam. *syn*-aldoxime and of the three nitrocinnam. *anti*aldoximes have been studied. The four *anti*-oximes with phenylcarbimide give carbanilino-compounds which, on hydrolysis with sodium hydroxide, regenerate the original oximes, and therefore the *anti*-configuration may be assigned to them. In no case is there any evidence of the primary formation of the *syn*-carbanilino-derivative as is the case with the action of phenylcarbimide on *m*-nitrobenz. *anti*aldoxime and on benz. *anti*aldoxime (compare Brady and Dunn, T., 1916, 109, 669). With cinnam. *syn*aldoxime in dry ethereal solution, phenylcarbimide gives an immediate precipitate of a bright yellow carbanilino-derivative which, on hydrolysis, yields cinnam. *anti*aldoxime. This compound dissolves slightly in most cold organic solvents, giving a yellow solution, but such solutions rapidly lose their colour, especially on warming, the compound being converted into a colour-

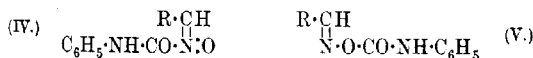
less form which also yields cinnamonnitrile on hydrolysis. Both these compounds, on keeping, decompose in a manner similar to other carbanilino-derivatives of *syn*-oximes studied by Dunn and one of us.

The formation of yellow and colourless forms of the carbanilino-derivatives from *syn*-aldoximes has been observed by Goldschmidt and van Rietschoten (*Ber.*, 1893, **26**, 2089) in the case of carbanilino-anis*syn*aldoxime and carbo-*o*-toluidinoanis*syn*aldoxime, but no explanation of the phenomenon has been suggested. The reaction does not appear to be a general one, and may be an intermediate stage in the formation of the cyclic structure of the carbanilino-derivatives of the *syn*-oximes which has been suggested by Dunn and one of us ( $I \rightarrow II$ , below).

As the shift in the absorption of oximino-compounds towards the visible end of the spectrum and consequent development of a yellow colour seem to be associated with a quinquivalent nitrogen atom (compare Brady, T., 1914, **105**, 2104), there is some reason for retaining such a nitrogen atom in the yellow carbanilino-compound. The theory previously propounded involves the oxime reacting in the tautomeric form (I) and addition taking place at the nitrogen-oxygen and nitrogen-carbon double bonds. If the first stage of the addition is at the nitrogen-oxygen double bond, the reaction would take place as follows :



formula III representing the unstable yellow carbanilino-compound. Another alternative would be the formation of the compound IV, but it seems unlikely that this would readily undergo isomeric change. The possibility that the yellow derivative has formula II and that the colourless compound is the normal carbanilino-derivative (V)

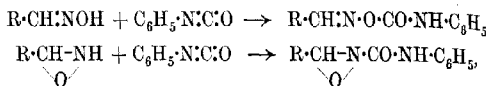


is open to two objections; first, there seems to be no reason why the cyclic compound should be coloured and, secondly, it has been shown (Brady and Dunn, *loc. cit.*) that the migration of the hydrogen atom in the cyclic compound and consequent reformation of the carbon-nitrogen double bond result in the inversion of the configuration of the resulting carbanilino-derivative. It must be confessed that these views are very speculative, but it is hoped to bring forward more experimental evidence at a later date.

While on this question, some mention must be made of a paper



by Atack (T., 1921, 119, 1175) in which certain statements are made which need refutation. This author states that "Brady and Dunn satisfactorily disposed of Goldschmidt's supposed proof of the structural identity of isomeric oximes by showing that phenylcarbimide gives identical compounds from both the *syn*- and *anti*-isomerides." This statement is misleading, and shows a lack of understanding of the subject. Goldschmidt's argument was that phenylcarbimide would probably react differently with the two oximes as formulated by Beckmann, giving in one case a carbanilino-derivative and in the other a substituted carbamide :



and that the latter compound would be more stable than are the carbanilino-derivatives of the *syn*-aldoximes. The work of Dunn and one of us showed that in certain cases "by the action of phenylcarbimide on the *anti*-oximes a certain quantity of carbanilino-*syn*-derivative is produced, if, indeed, this compound is not the primary product of the reaction." It was found that *p*-dimethylamino-benzantialdoxime and 3:4-dimethoxybenzantialdoxime gave almost exclusively a *syn*-carbanilino-derivative, but under similar conditions *o*- and *m*-nitrobenzantialdoximes and benzantialdoximes gave a mixture of the *anti*- and *syn*-derivatives, and it has now been shown that cinnamantialdoxime and its three nitro-derivatives give *anti*-carbanilino-derivatives. This does not invalidate Goldschmidt's argument against the Beckmann formula, and certainly confirms rather than disproves the identity of structure of the isomeric oximes. Indeed, it is very difficult to explain the action of phenylcarbimide and many other reagents, unless it is assumed with Dunn and one of us that the oximes exist in stereoisomeric forms and also react in the tautomeric forms

$$\begin{array}{cc} \text{R}\cdot\text{CH} & \text{R}\cdot\text{CH} \\ \text{O}\cdot\text{NH} & \text{HN}\cdot\text{O} \end{array}$$

The claim made in previous papers was that the use, suggested by Goldschmidt, of phenylcarbimide as an agent for the determination of the configuration of oximes was not satisfactory. Atack also criticises the explanation put forward of the mechanism of the formation of the *syn*-carbanilino-derivative from the *anti*-oxime. He objects that the suggestion is scarcely an explanation, as it merely assumes that phenylcarbimide first converts the *anti*- into the *syn*-isomeride. That such conversion takes place was the whole point of the argument brought forward, namely, that under the influence of additive reagents, for example, hydrogen chloride or phenylcarbimide, the carbon-nitrogen double bond was ruptured, resulting

in some cases in inversion of the configuration of the oxime. Experimental work bearing on this question and on other criticisms of Atack is in hand, and will be made the subject of a further communication.

#### EXPERIMENTAL.

*Cinnamanti- and Cinnamsyn-aldoxime.*—The original method of Bamberger and Goldschmidt (*loc. cit.*) was slightly modified as regards temperature and time of reaction, as it was found that by this means a less resinous product was obtained. Twenty-six grams of freshly distilled cinnamaldehyde were added to 250 c.c. of water followed by 14 grams of hydroxylamine hydrochloride in 50 c.c. of water and 24 grams of sodium hydroxide in 100 c.c. of water, and the mixture was shaken. Reaction took place at once and the oil dissolved as the sodium salt of the oxime. After remaining for two hours, the solution was saturated with carbon dioxide, the oily precipitated oxime extracted with ether, the ethereal solution dried over anhydrous sodium sulphate and allowed to evaporate spontaneously. In this way, there was obtained a mixture of the *anti*- and *syn*-isomerides. The mixture was extracted with boiling light petroleum, and from the decanted solvent, on cooling, crude cinnamantialdoxime separated as a white, crystalline powder. After filtering off the precipitate, the petroleum was again used for extraction of the residue, three extractions in all being given. The product from the last extraction was, however, much contaminated with the *syn*-oxime. The residue was then worked up for cinnamsyn-aldoxime by crystallisation from benzene. The crude *anti*-oxime melted in the neighbourhood of 64°, as stated by Bamberger and Goldschmidt, but not at all sharply. Crystallisation from light petroleum did not improve the purity of the compound to any appreciable extent. The difficulty in purification is explicable by the fact that cinnamsynaldoxime is appreciably soluble in boiling light petroleum and being less soluble than the *anti*-isomeride in the cold solvent, it separates out with it.

The amount of *anti*-oxime isolated by this process was small and indicated that the amount present in the mixture was less than would be anticipated from its low melting point. It seemed possible that another compound was present, especially in view of the large quantity of resinous material obtained on evaporating the benzene after crystallising out the *syn*-oxime. The formation of resinous substances seems to be a usual concomitant of reactions with cinnamaldehyde, and may be due to polymerisation under the influence of alkali. It was noticed that in the absence of alkali a cleaner product was obtained (see below); no success, however, has attended efforts to isolate other compounds. Attempts to increase

the quantity of *anti*-oxime formed by carrying out the oximation as above at 0° or by acting on the aldehyde with free hydroxylamine in alcohol or pyridine solution were unsuccessful.

The best method for preparing pure cinnamantialdoxime consists in hydrolysing benzoylcinnamantialdoxime, which may be prepared from the oximation mixture (see below). The benzoyl compound was heated on the water-bath for an hour with excess of 2*N*-sodium hydroxide, when a clear solution was obtained. After cooling, this was saturated with carbon dioxide, the precipitated oxime dissolved in a small quantity of alcohol, and the cold solution poured into four times its volume of water with vigorous stirring, when cinnamantialdoxime separated in colourless needles melting at 76°.

For the preparation of cinnamsynaldoxime, a modification of Beckmann's method (*Annalen*, 1909, **365**, 261) was found to be the most satisfactory. The aldehyde was dissolved in alcohol, and slightly more than one molecular proportion of hydroxylamine hydrochloride in concentrated aqueous solution added. After leaving for twenty-four hours in a stoppered bottle at room temperature, the solution was diluted, the precipitated oxime dried, extracted several times with light petroleum to remove any of the *anti*-isomeride, and crystallised from the minimum amount of boiling benzene. Many solvents were tried, but benzene proved to be the only satisfactory one; excess of solvent must be avoided or great loss of yield results, as the oxime is moderately soluble in the cold benzene. Addition of light petroleum to lessen the solubility results in a less pure product being obtained.

*Benzoylcinnamantialdoxime*,  $C_6H_5\cdot CH:CH\cdot CH:NO\cdot CO\cdot C_6H_5$ .—Seven grams of cinnamsynaldoxime, or of the mixture of oximes obtained in the oximation of cinnamaldehyde, were stirred into 28 grams of benzoyl chloride in small portions at a time, care being taken to avoid rise in temperature. The mixture was added to 200 c.c. of 2*N*-sodium hydroxide and shaken vigorously for thirty minutes. The lumps which formed were broken up and left in contact with the alkali over-night. The solid was separated, washed with water, and crystallised from alcohol, when benzoylcinnamantialdoxime separated in long, white needles melting at 122° (Found: C = 76.3; H = 5.3. Calc., C = 75.6; H = 5.2 per cent.). This compound is obviously that obtained by Bornemann (*Ber.*, 1886, **19**, 1512) and described in Richter's "Lexicon" as benzoylcinnamsynaldoxime.

*Carbanilinocinnamantialdoxime*,  $CHPh\cdot CH:CH:NO\cdot CO\cdot NHPh$ .—Three grams of cinnamantialdoxime were dissolved in 50 c.c. of dry ether, 2.4 grams of phenylcarbimide in 50 c.c. of dry ether added, and the solution left over-night in a stoppered bottle. No solid

separated, so the ether was removed in a vacuum desiccator at room temperature. A yellow solid remained which was somewhat oily and was purified by crystallisation from benzene and light petroleum, when the carbanilino-compound separated as almost white, rectangular crystals melting and decomposing at  $138^{\circ}$  (Found: N = 10.4.  $C_{16}H_{14}O_2N_2$  requires N = 10.5 per cent.).

The carbanilino-compound was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide for an hour, when almost the whole of the solid had dissolved; the solution was diluted somewhat, filtered, extracted with ether to remove aniline and diphenylcarbamide formed from the decomposition of the phenylcarbamie acid, and the aqueous solution saturated with carbon dioxide. An oily precipitate was obtained which was extracted with ether; after removing the solvent at room temperature, an oil was obtained which, on keeping and scratching, solidified and after crystallisation from light petroleum was found to be the original *cinnamantialdoxime* by its melting point and mixed melting point with that compound.

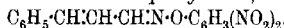
*Carbanilino-cinnamantialdoxime*.—*Cinnamantialdoxime* was dissolved in dry ether, and phenylcarbimide (1 mol.) in dry ether added. A carbanilino-compound was at once precipitated as a bright yellow compound. This was filtered off, washed thoroughly with ether, and dried on a porous plate. Thus obtained, it consisted of a bright yellow, micro-crystalline powder melting at  $76^{\circ}$ ; it dissolved slightly in cold alcohol or acetone to a yellow solution which completely lost its colour on gentle warming. On boiling with alcohol, the yellow compound dissolved to a colourless solution which, on cooling, deposited a white carbanilino-derivative melting and decomposing at  $84^{\circ}$ . All attempts to crystallise the yellow compound were unsuccessful owing to the readiness with which it changed into the white derivative; however, its method of preparation makes it reasonable to suppose that it was fairly pure.

Both white and yellow compounds were hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide. Some ammonia was evolved and an oil mixed with solid remained suspended in the liquid. The mixture was cooled, diluted, and extracted with ether; on acidifying the alkaline solution, a faint opalescence was obtained, but no oxime was found. The ether extract was evaporated, when an oil and a solid were obtained; the oil was removed by washing with a little alcohol, and the solid found to be diphenylcarbamide. The alcoholic solution was found to contain aniline and, on heating with 30 per cent. sodium hydroxide solution, ammonia was evolved and cinnamic acid obtained after acidification, indicating the presence of cinnamitrile in the oil. Both yellow and white compounds, on keeping even in the dark, decompose giving aniline,

diphenylcarbamide, and cinnamionitrile. They behave, therefore, in an analogous manner to other carbanilino-*syn*aldoximes (compare Brady and Dunn, T., 1916, **109**, 655).

Yellow compound, Found : N = 10.5; *M* (by depression of freezing point of naphthalene) = 249. White compound, Found : N = 10.7.  $C_{16}H_{14}O_2N_2$  requires N = 10.5 per cent.; *M* = 266.

*Cinnamantialdoxime-2:4-dinitrophenyl Ether*,



—Two grams of cinnamantialdoxime, extracted from the oximation mixture by the method of Bamberger and Goldschmidt, were dissolved in 20 c.c. of alcohol together with 1 gram of 2:4-dinitrochlorobenzene and heated on the water-bath; 6 c.c. of 10 per cent. sodium hydroxide were then added, when a dark coloration was instantly produced and after a few seconds the dinitrophenyl ether separated. This was collected, washed with alcohol, in which it is very sparingly soluble, and crystallised from boiling acetone, when it was obtained as a pale yellow, crystalline powder melting and decomposing, when rapidly heated, at 188° (Found : N = 13.4.  $C_{15}H_{11}O_3N_3$  requires N = 13.4 per cent.). The same compound was formed from the cinnamantialdoxime obtained by hydrolysis of the benzoyl compound.

*Cinnamantialdoxime-O-benzyl Ether*,  $CHPh\cdot CH:CH\cdot N\cdot O\cdot CH_2Ph$ .

—2.4 Grams of cinnamantialdoxime, obtained both from the crude oximation mixture and by hydrolysis of the benzoyl compound, were dissolved in alcohol, 0.37 gram of sodium dissolved in alcohol was added together with 2 grams of benzyl chloride, and the mixture boiled under reflux for thirty minutes. Excess of water was added and the oil which separated extracted with ether. On removing the solvent, the residue slowly solidified, and after pressing on a porous plate to free from oil it was crystallised from alcohol, when the *O*-benzyl ether separated in colourless, rectangular plates melting at 88° (Found : N = 5.9.  $C_{16}H_{15}ON$  requires N = 5.9 per cent.).

Equimolecular amounts of cinnamaldehyde, sodium ethoxide, and  $\alpha$ -benzylhydroxylamine hydrochloride in alcohol were left at room temperature for seventy-two hours. The solution was diluted somewhat and the solid which separated crystallised three times from alcohol, when cinnamantialdoxime-*O*-benzyl ether separated; it was shown to be identical with the compound prepared above by its melting point and mixed melting point with that compound. The original mother-liquor, on keeping, deposited a few crystals melting at 123°, which may be the cinnamsynaldoxime-*O*-benzyl ether, but the amount was insufficient for further investigation. Several attempts have been made to prepare the *syn*-derivative by the action of benzyl chloride on the silver salt of cinnamsynaldoxime,

but without success. The silver salt rapidly blackens and in most cases only an uncrystallisable oil was obtained, although in one experiment cinnamantialdoxime-*O*-benzyl ether was isolated from the product.

*Cinnamaldoxime-N-benzyl Ether*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}(\text{O})\cdot\text{CH}_2\text{Ph}$ .—A mixture of 4 grams of cinnamsynaldoxime, 3.5 grams of benzyl chloride, and 1.1 grams of sodium hydroxide in alcoholic solution was boiled under reflux for thirty minutes. On diluting with water, a milky emulsion was obtained which, on vigorous stirring, deposited a brown, somewhat oily solid. This was separated, washed with a small quantity of ether, and the clean yellow solid which remained crystallised from alcohol, when the *N*-benzyl ether was obtained in very pale yellow, glistening plates melting at  $130^\circ$ . This compound is obviously identical with the *N*-benzyl ether of cinnamaldoxime prepared by Neubauer (*Annalen*, 1897, 298, 192) by the action of  $\beta$ -benzylhydroxylamine on cinnamaldehyde.

*m-Nitrocinnamantialdoxime*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{NOH}$ .—Five grams of *m*-nitrocinnamaldehyde were suspended in 100 c.c. of alcohol, 2 grams of hydroxylamine hydrochloride in a minimum amount of water added, followed by 30 c.c. of 10 per cent. sodium hydroxide. The aldehyde dissolved rapidly and after an hour the mixture was diluted and the oxime precipitated with dilute hydrochloric acid. Crystallised from alcohol, the oxime separated in yellow, rectangular plates melting at  $157^\circ$  (Found:  $\text{N} = 14.8$ .  $\text{C}_9\text{H}_9\text{O}_3\text{N}_2$  requires  $\text{N} = 14.6$  per cent.). Search in the mother-liquor from the crystallisation failed to show the presence of an isomeride. The oxime was also prepared by Beckmann's method (*loc. cit.*) by warming at  $60^\circ$  equimolecular amounts of the aldehyde and hydroxylamine hydrochloride for some hours in alcoholic solution. This method usually gives the *syn*-isomeride where one is obtainable, but on cooling the mixture and pouring into sodium carbonate solution the *anti*-oxime was again obtained.

*Acetyl-m-nitrocinnamantialdoxime*,  $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ .—The above oxime was dissolved in acetic anhydride at  $30^\circ$  and the excess of anhydride decomposed by the addition of a large excess of sodium carbonate solution. The solid which separated was crystallised from alcohol, when the acetyl compound separated as pale lemon-coloured plates melting at  $136^\circ$  (Found:  $\text{N} = 12.2$ .  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{N} = 12.0$  per cent.). On hydrolysis by heating on the water-bath with 2*N*-sodium hydroxide, the original oxime was regenerated, showing that it possessed the *anti*-configuration.

*m-Nitrocinnamonitrile*.—Five grams of *m*-nitrocinnamantialdoxime were boiled under reflux with 25 c.c. of acetic anhydride for an hour. After cooling, the excess of anhydride, was decomposed by shaking

with sodium carbonate solution, and the precipitated nitrile crystallised from alcohol with the addition of a little animal charcoal. *m*-Nitrocinnamonitrile forms pale yellow needles melting at  $160^{\circ}$  (Found:  $N = 16.2$ .  $C_9H_8O_2N_2$  requires  $N = 16.1$  per cent.). In this preparation, it is not sufficient to heat on the water-bath as in many other cases for the preparation of nitriles from oximes. In these circumstances, the acetyl derivative of the oxime is formed, which is unusually stable.

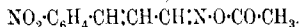
*Carbanilino-m-nitrocinnamantialdoxime.*



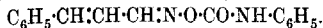
—To a solution of 1.6 grams of *m*-nitrocinnamantialdoxime in 120 c.c. of dry ether, 1 gram of phenylcarbinide was added. After leaving for two days in the dark, practically all the carbanilino-derivative had crystallised out in large, hexagonal crystals. These were removed, washed with ether, and found to melt and decompose at  $137^{\circ}$ . On crystallisation from alcohol, the compound was obtained in pale yellow needles melting and decomposing at  $140^{\circ}$ . No change in configuration seems to take place during recrystallisation (Found:  $N = 13.7$ .  $C_{16}H_{13}O_4N_3$  requires  $N = 13.5$  per cent.). The compound was hydrolysed by heating on the water-bath for thirty minutes with 2*N*-sodium hydroxide. Aniline was recognised by its odour and, after cooling, carbon dioxide precipitated the original oxime.

*o*-Nitrocinnamantialdoxime,  $NO_2 \cdot C_6H_4 \cdot CH:CH \cdot CH:NOH$ .—Equivalent quantities of *o*-nitrocinnamaldehyde and hydroxylamine hydrochloride in alcohol were heated at  $60^{\circ}$  for three hours. The solution was diluted with water, and the precipitated oxime crystallised from alcohol, when it separated as fawn-coloured, pearly leaflets melting at  $134^{\circ}$  (Found:  $N = 14.6$ .  $C_9H_8O_3N_2$  requires  $N = 14.6$  per cent.). An alternative and quicker method of preparation consisted in dissolving 5 grams of sodium hydroxide in 50 c.c. of water and adding thereto 2.5 grams of hydroxylamine hydrochloride in a little water. The solution was then added to 5 grams of *o*-nitrocinnamaldehyde suspended in 25 c.c. of water, and the mixture shaken for ten minutes, when a clear orange solution was obtained; this was diluted with an equal volume of water, and the oxime precipitated with carbon dioxide.

*Acetyl-o-nitrocinnamantialdoxime.*



—This compound, prepared from *o*-nitrocinnamantialdoxime in an analogous way to the *m*-derivative, crystallises from benzene in white crystals melting at  $107^{\circ}$  (Found:  $N = 12.0$ .  $C_{11}H_{10}O_4N_2$  requires  $N = 12.0$  per cent.). On hydrolysis in the usual way, the original oxime was regenerated, thus establishing the *anti*-configuration of the latter.

*Carbanilino-o-nitrocinnamantialdoxime*,

—To a solution of 1.6 grams of *o*-nitrocinnamantialdoxime in 70 c.c. of dry ether, 1 gram of phenylcarbimide was added, when the liquid became deep yellow, but no solid separated. After leaving overnight, the ether was evaporated in a vacuum and a yellow oil obtained which soon solidified. The solid was crystallised from alcohol, when the carbanilino-compound separated as a bright yellow, crystalline powder melting at  $104^\circ$  and decomposing below  $110^\circ$  (Found:  $\text{N} = 13.7$ .  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}_3$  requires  $\text{N} = 13.5$  per cent.). On hydrolysis as in the case of the *m*-derivative, the original oxime was produced.

*p*-Nitrocinnamantialdoxime.—This compound has been prepared by Einhorn and Gehrenbeck (*Annalen*, 1889, **253**, 349), but its configuration has not been determined. These workers treated the aldehyde in alcohol with hydroxylamine hydrochloride and sodium carbonate. It was found, however, that a cleaner product was obtained by using the method of Beckmann and thus avoiding the presence of alkali. Although this method is usually employed to obtain the *syn*-oxime, in this case the same compound as that obtained by Einhorn and Gehrenbeck was formed, which proved to be the *anti*-oxime by the behaviour of its acetyl derivative on hydrolysis. Equimolecular quantities of the aldehyde and hydroxylamine hydrochloride were heated in alcoholic solution at  $50^\circ$  for three hours, the oxime was precipitated by dilution, and crystallised from alcohol.

*Acetyl-p*-nitrocinnamantialdoxime.—This compound, prepared in the usual way, crystallises from alcohol in deep yellow octahedra melting at  $158^\circ$  (Found:  $\text{N} = 12.3$ .  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$  requires  $\text{N} = 12.0$  per cent.). On hydrolysis, it regenerates the original oxime.

*p*-Nitrocinnamonitrile.—This compound, prepared in an analogous way to the *m*-nitro-derivative, crystallises from alcohol in yellowish-brown needles melting at  $202^\circ$  (Found:  $\text{N} = 16.4$ .  $\text{C}_9\text{H}_6\text{O}_2\text{N}_2$  requires  $\text{N} = 16.1$  per cent.).

*Carbanilino-p*-nitrocinnamantialdoxime. — *p*-Nitrocinnamantialdoxime was dissolved in dry ether, and phenylcarbimide (1 mol.) added. On keeping, the carbanilino-compound separated as yellow crystals which, after washing with dry ether and crystallising from benzene, melted at  $133^\circ$  (Found:  $\text{N} = 13.8$ .  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}_3$  requires  $\text{N} = 13.5$  per cent.). This compound was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide. The clear solution obtained was saturated with carbon dioxide, when *p*-nitrocinnamantialdoxime was precipitated. During the hydrolysis, a small amount of ammonia was evolved and on acidifying the carbonate solution a little *p*-nitrocinnamic acid was precipitated. There



appears, therefore, to be some nitrile formed during the hydrolysis which is further decomposed; as, however, almost all the carbanilino-derivative was hydrolysed to the oxime, there can be little doubt of its configuration.

The authors wish to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the cost of this work, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (C. D. T.).

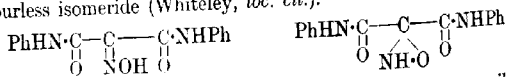
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[Received, July 27th, 1922.]

CCLII.—*The Oxime of Mesoxamide (isoNitrosomalonal-  
amide) and some Allied Compounds. Part IV. The  
Ethers of isoNitrosomalonanilide, isoNitrosomalon-  
dimethylamide, and isoNitrosomalondibenzylamide.*

By ARTHUR GEOFFREY RENDALL and MARTHA ANNIE WHITELEY.

It was shown by one of us (Whiteley, T., 1903, **83**, 24) that the aryl-substituted derivatives of isonitrosomalonalamide, notably isonitrosomalonanilide, exist in two isomeric forms, differing in colour and solubility but mutually convertible by heating, by the action of solvents, and by the action of acids on solutions of the alkali salts. Similar isomerism has been observed in other isonitroso-compounds, a striking example being afforded by the isonitroso-derivatives of camphor and epicamphor, each of which has been shown by Forster (T., 1912, **103**, 664) to exist in two forms, one stable and the other labile; in these cases, the isomerism has been shown conclusively to be stereochemical, the stable forms being the *syn*- and the labile forms the *anti*-oximes. Since the molecule in isonitrosomalonanilide is symmetrical with respect to the carbon atom associated with the isonitroso- or oximino-group, the isomerism in this series cannot be geometrical, and must be due to structural differences in the molecules of the two isomerides. The simplest explanation, based on the fact that one isomeride is coloured and the other colourless, represents them as having the oxime and isooxime structure respectively, the coloured compound having the conjugated double linkage that is not present in the colourless isomeride (Whiteley, *loc. cit.*).



*Yellow isonitrosomalonanilide. Colourless isonitrosomalonanilide.*

If this is the correct explanation of the isomerism occurring in this series of *isonitroso*-compounds, the ethers might be expected to exhibit similar isomerism, the coloured isomeride yielding an oxygen and the colourless isomeride a nitrogen ether, and these on hydrolysis should yield the  $\alpha$ - and  $\beta$ -alkylhydroxylamine, respectively, as was obtained by Beckmann (*Ber.*, 1889, 22, 537, 1521) in the case of the isomeric benzyl ethers of benzald-oxime.

By the action of the alkyl iodide on *isonitrosomalonanilide* in benzene solution and in the presence of dry silver oxide, *colourless* ethers were the only products and the yield was about 85 per cent. of that theoretically possible. The ethers were precipitated from the benzene medium in association with the silver iodide as greenish-yellow to orange solids, insoluble and stable in benzene, ether, or petroleum, but decomposed by boiling alcohol, yielding a solution of the ether and a residue of silver iodide. The methyl, ethyl, *n*- and *iso*-propyl, and *n*-butyl ethers of *isonitrosomalonanilide* were prepared by this method; they are well-defined, crystalline, colourless compounds, the melting point becoming lower, but the stability of the double compound with silver iodide increasing, as the series is ascended (see table).

In the preparation of the ethers of *isonitrosomalondimethylamide* by the same method, it was found that the methyl, ethyl, and *isopropyl* ethers were insoluble in benzene, but did not form double compounds with the silver iodide, the precipitate being a grey, heterogeneous mixture of the silver iodide and oxide with the colourless crystalline ether. The *n*-propyl and *n*-butyl ethers, on the other hand, remained in solution in the benzene, from which they were extracted by water. With the exception of the ethyl compound, the melting points of the ethers of *isonitrosomalondimethylamide* become lower as the series is ascended (see table).

The methyl and ethyl ethers of *isonitrosomalondibenzylamide*, similarly prepared by the silver oxide and alkyl iodide method, did not form double compounds with the silver iodide, but remained in solution in the benzene, and were isolated by evaporation of the solvent and subsequent crystallisation. These ethers are also colourless and the ethyl ether has the lower melting point (see table).

Ether.	M. p. of ethers of <i>isonitrosomalonanilide</i> .	M. p. of ethers of <i>isonitrosomalondimethylamide</i> .	M. p. of ethers of <i>isonitrosomalondibenzylamide</i> .
Methyl .....	194°	131°	83.5°
Ethyl .....	166	133	73.5
<i>n</i> -Propyl .....	156	94	
<i>iso</i> Propyl .....	170	128	
<i>n</i> -Butyl .....	138.5	66	

As the ethers of these isonitroso-compounds prepared by the silver oxide method—that is potentially through the silver salt—showed no isomerism, attempts were made to prepare the methyl ethers by the action of diazomethane, and in the case of isonitrosomalonanilide the colourless ether, m. p.  $194^{\circ}$ , and also an isomeric yellow ether, m. p.  $147^{\circ}$  (decomp.), were obtained. The yellow ether is unstable and readily converted into the colourless isomeride by the action of solvents, whilst the converse change cannot be brought about. The relative amounts of the two forms of the ether are the same whether the yellow or colourless isomeride of isonitrosomalonanilide is thus methylated, but are influenced by the nature of the solvent in which the reaction takes place; in alcoholic solution, the product is a mixture of the yellow and colourless isomerides, whilst in ether solution the yellow ether is the sole product.

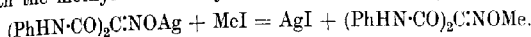
All attempts to prepare the methyl ether of isonitrosomalondimethylamide by the action of diazomethane were unsuccessful. On adding the ethereal solution of diazomethane to the isonitroso-compound suspended in ether, there was a vigorous evolution of nitrogen, indicating that methylation was taking place, but the product was a syrup with a green fluorescence from which no definite compound could be isolated. It gave the yellow alkali and purple ferrous salts characteristic of the isonitroso-compounds of this series, and may be possibly isonitrosomalontetramethylamide,  $(\text{CO-NMe}_2)_2\text{C}^{\cdot}\text{NOH}$ , as it resembles the crude product obtained by the action of nitrosyl chloride on the condensation product of malonyl chloride with dimethylamine.

The value of methyl sulphate as a methylating agent on compounds of the isonitroso-type was also studied; in the case of isonitrosomalonanilide, it was found that the potassium salt, in the presence of potassium carbonate, was readily converted into the methyl ether by the action of methyl sulphate at the ordinary temperature, the colourless ether, m. p.  $194^{\circ}$ , being the sole product.

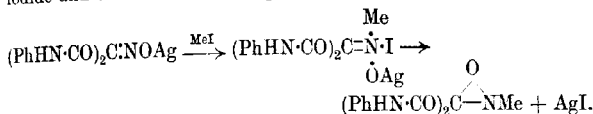
The foregoing results indicate that only those isonitroso-derivatives of the substituted malonamides that exhibit isomerism yield isomeric forms of ethers, for in the three cases studied, isonitrosomalonanilide, that exists in a colourless and in a yellow form, yields a colourless and a yellow methyl ether; whilst isonitrosomalondimethylamide and isonitrosomalondibenzylamide, known only in the colourless forms, yield only colourless methyl ethers.

The extension of the investigation to the ethers of those isonitroso-derivatives of the substituted malonamides in which the yellow isomeride is more stable than the colourless form has led to such far-reaching results that these will form the subject of a separate communication.

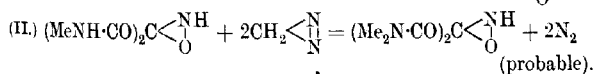
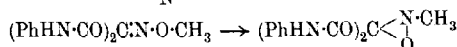
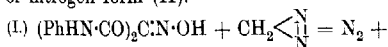
Assuming that the difference in structure between the yellow and colourless ethers of *isonitrosomalonanilide* is similar to that suggested for the two forms of the *isonitroso*-compound itself, namely, that the yellow ether is the oxygen and the colourless ether the nitrogen ether, it might be regarded as anomalous that the colourless ether should be produced by the action of methyl iodide on the *isonitroso*-compound in the presence of silver oxide, for presumably the silver salt,  $(\text{PhHN}\cdot\text{CO})_2\text{C}\cdot\text{NOAg}$ , would be formed first, and this should interact by double decomposition with the methyl iodide to yield the coloured or oxygen ether:



In this connexion, it is important to remember that the colourless ether was not obtained directly; the first product of the reaction was a yellow double compound of the ether with silver iodide, which was decomposed by boiling with alcohol. It is probable, therefore, that this compound is an additive compound of the silver salt with methyl iodide, which is stable in benzene and other non-hydroxylic solvents, but decomposed by alcohol to yield silver iodide and the colourless nitrogen ether according to the equations

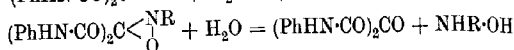
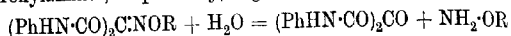


The yellow or oxygen ether is the sole product when diazomethane reacts with *isonitrosomalonanilide* in dry ether solution, in which solvent the yellow form of the *isonitroso*-compound is the more stable, whilst in alcoholic solution a mixture of the yellow *O*-ether and the colourless *N*-ether is obtained. Since, however, the *O*-ether is very unstable and readily converted by the action of alcoholic solvents into the *N*-ether, it is probable that the yellow or *O*-ether is the sole product of the reaction between *isonitrosomalonanilide* and diazomethane, the colourless or *N*-ether arising from subsequent isomerisation in the alcoholic solution (I). This is the more probable seeing that diazomethane appears to have no methylating action on the *isonitroso*-group of *isonitrosomalondimethylamide*, which exists only in the colourless or nitrogen form (II).

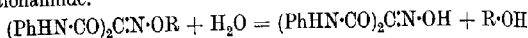


*Hydrolysis of isoNitrosomalonanilide and its Ethers.*

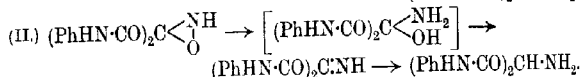
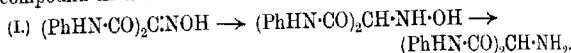
It was hoped that the hydrolysis of the ethers of isonitrosomalonanilide would throw some light on the structure of these compounds, the *O*- and *N*-ethers yielding the corresponding  $\alpha$ - and  $\beta$ -alkyl-hydroxylamines, respectively, together with mesoxanilide :



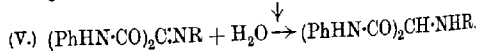
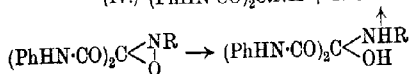
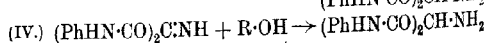
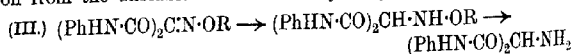
Experiment showed, however, that isonitrosomalonanilide does not yield hydroxylamine, nor its ethers the alkyl derivatives of hydroxylamine, on hydrolysis. *iso*Nitrosomalonanilide is remarkably stable towards hydrolysing agents, and prolonged heating with acids causes profound decomposition. The ethers behave like the esters of weak acids on hydrolysis, yielding the alcohol and isonitrosomalonanilide.

*Reduction of isoNitrosomalonanilide and its Ethers.*

It might be expected that the two forms of isonitrosomalonanilide would yield the same product, *aminomalonanilide*, on complete reduction, with the intermediate formation of the *hydroxylamino*-compound in the case of the coloured or *O*-form (I), and of the *imino*-compound in the case of the colourless or *N*-form (II) :



On the other hand, the *O*-form of the ether should yield *alkyloxyaminomalonanilide* on partial and *aminomalonanilide* on complete reduction (III); whilst the *N*-form of the ether should furnish *alkyliminomalonanilide* or *iminomalonanilide* as the intermediate compound, and *alkylaminomalonanilide* or *aminomalonanilide* as the final product, according as water (IV) or alcohol (V) were split off from the unstable intermediate hydroxy-compound :



The behaviour of isonitrosomalonanilide and its ethers towards a large number of reducing agents, acid, alkaline, and neutral, was examined; the compounds were reduced very smoothly, but the results obtained failed to throw any further light on the question of the constitution of the original compounds; in no case could any pure intermediate compound be isolated, and the final product was always *aminomalonanilide* (Whiteley, P., 1904, 20, 92).

#### EXPERIMENTAL.

##### I.—Preparation of the Ethers of isoNitrosomalonanilide by the Action of the Alkyl Iodide in the Presence of Silver Oxide.

Ten grams of isonitrosomalonanilide (1 mol.) were suspended in 200 c.c. of dry benzene containing the alkyl iodide (3 mols.) in solution, 12.5 grams (1.5 mols.) of dry silver oxide were then added in many small portions, the mixture being well shaken after each addition. There was a slight rise in temperature and the formation of a copious yellowish-green precipitate. After remaining at the ordinary temperature during twelve hours, the mixture was filtered, the precipitated double compound of the ether with silver iodide drained on porous earthenware until free from benzene, boiled with absolute alcohol for about fifteen minutes, and filtered. The residue consisted of silver iodide with the slight excess of silver oxide, and the filtrate, on cooling, deposited the ether in a crystalline form, the portion remaining in solution being precipitated on dilution with water. The yield is about 85 per cent. of that theoretically possible. The solubility of the ethers in all the ordinary organic solvents increases with the complexity of the alkyl group, and they all crystallise well from formic acid.

*Methyl ether of isonitrosomalonanilide* (colourless form),  $(\text{PhHN}\cdot\text{CO})_2\text{C}\begin{smallmatrix} \text{NMe} \\ \diagdown \\ \text{O} \end{smallmatrix}$ , is sparingly soluble in ethyl or methyl alcohol, ethyl acetate, benzene, petroleum (b. p. 100–120°), or chloroform; readily soluble in acetone, or formic or acetic acid, and insoluble in ether. It crystallises in stout, colourless prisms, m. p. 194° (Found: N = 14.18, 14.17.  $\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_3$  requires N = 14.14 per cent.).

*Ethyl ether of isonitrosomalonanilide* (colourless form),  $(\text{PhHN}\cdot\text{CO})_2\text{C}\begin{smallmatrix} \text{NEt} \\ \diagdown \\ \text{O} \end{smallmatrix}$ , is soluble in cold methyl alcohol, ethyl acetate, acetone, or chloroform; readily soluble in ethyl alcohol, formic or acetic acid, benzene, or petroleum (b. p. 100–120°), and very sparingly soluble in ether or petroleum (b. p. 60–80°). It crystallises in wheatsheaf clusters of thin prisms, m. p. 166° (Found: N = 13.58.  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3$  requires N = 13.5 per cent.).

*isoPropyl ether of isonitrosomalonanilide* (colourless form),  $(\text{PhHN}\cdot\text{CO})_2\text{C} < \begin{smallmatrix} \text{NPr}^s \\ \text{O} \end{smallmatrix}$ , closely resembles the ethyl ether in solubility. It crystallises in felted masses of very thin needles, m. p.  $170^\circ$  (Found : N = 13.00.  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}_3$  requires N = 12.92 per cent.).

*n-Propyl ether of isonitrosomalonanilide* (colourless form),  $(\text{PhHN}\cdot\text{CO})_2\text{C} < \begin{smallmatrix} \text{NPr}^a \\ \text{O} \end{smallmatrix}$ , is soluble in cold ethyl or methyl alcohol, ethyl acetate, acetone, chloroform, or benzene, readily soluble in formic or acetic acid, and sparingly soluble in ether, or the petroleum (b. p.  $60\text{--}80^\circ$  or  $100\text{--}120^\circ$ ). It crystallises from formic acid in felted masses of thin, prismatic needles, or from petroleum in minute, stout prisms, m. p.  $156^\circ$  (Found : N = 12.96.  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}_3$  requires N = 12.92 per cent.).

*n-Butyl ether of isonitrosomalonanilide* (colourless form),  $(\text{PhHN}\cdot\text{CO})_2\text{C} < \begin{smallmatrix} \text{N}\cdot\text{C}_4\text{H}_9 \\ \text{O} \end{smallmatrix}$ , is soluble in cold ethyl or methyl alcohol, ethyl acetate, acetone, acetic acid, chloroform, or benzene; readily soluble in formic acid or petroleum (b. p.  $100\text{--}120^\circ$ ); and sparingly soluble in ether or petroleum (b. p.  $60\text{--}80^\circ$ ). It crystallises in well-formed, thin prisms, m. p.  $136.5^\circ$  (Found : N = 12.60.  $\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}_3$  requires N = 12.4 per cent.).

## II.—Preparation of the Ethers of isoNitrosomalondimethylamide by the Action of the Alkyl Iodide in the Presence of Silver Oxide.

Five grams of isonitrosomalondimethylamide (1 mol.), suspended in 100 c.c. of dry benzene containing the alkyl iodide (3 mols.) in solution, were treated gradually and with constant shaking with 11.5 grams (1.5 mols.) of dry powdered silver oxide. The mixture became warm, and after remaining for twelve hours at the ordinary temperature it was filtered. In the cases of the methyl, ethyl, and isopropyl compounds, the grey precipitate was a mixture of the colourless ether with the silver iodide and the excess of silver oxide, from which the ether was extracted by means of warm alcohol. The *n*-propyl and *n*-butyl ethers were not precipitated with the silver iodide, but remained in solution in the benzene, from which they were extracted by means of water. The yield of the ether is about 80 per cent. of that theoretically possible.

The ethers obtained by this method are colourless, crystalline compounds and are probably the *isooxime* ethers,  $(\text{MeHN}\cdot\text{CO})_2\text{C} < \begin{smallmatrix} \text{NR} \\ \text{O} \end{smallmatrix}$ .

*Methyl ether of isonitrosomalondimethylamide* (colourless form),  $(\text{MeHN}\cdot\text{CO})_2\text{C}(\text{NOMe})$ , dissolves readily in cold ethyl or methyl

alcohol, acetone, ethyl acetate, formic or acetic acid, chloroform, or water, and is sparingly soluble in ether, benzene, or petroleum (b. p. 100—120°). It crystallises in stout prisms, m. p. 131° (Found: N = 24.36.  $C_6H_{11}O_3N_3$  requires N = 24.28 per cent.).

*Ethyl ether of isonitrosomalondimethylamide* (colourless form),  $(MeHN\cdot CO)_2C(NOEt)$ , dissolves readily in cold ethyl or methyl alcohol, ethyl acetate, acetone, formic or acetic acid, chloroform, benzene or water, and is sparingly soluble in petroleum (b. p. 100—120°), and insoluble in ether or petroleum (b. p. 60—80°). It crystallises in well-formed, rhombic prisms having a fibrous fracture and melting at 133° (Found: N = 22.33.  $C_7H_{13}O_3N_3$  requires N = 22.4 per cent.).

*isoPropyl ether of isonitrosomalondimethylamide* (colourless form),  $(MeHN\cdot CO)_2C(NOPr^i)$ , is readily soluble in the cold in all the ordinary organic solvents, with the exception of benzene and petroleum (b. p. 100—120°), in which it is sparingly soluble, and ether, in which it is insoluble. It crystallises in stellate clusters of flattened prisms melting at 128° (Found: N = 21.30.  $C_8H_{15}O_3N_3$  requires N = 21.02 per cent.).

*n-Propyl ether of isonitrosomalondimethylamide* (colourless form),  $(MeHN\cdot CO)_2C(NOPr^e)$ , dissolves readily in the cold in water and in all the ordinary organic solvents with the exception of ether, in which it is insoluble. It can be crystallised from a mixture of amyl alcohol and light petroleum, and forms thin, prismatic needles melting at 94° (Found: N = 21.14.  $C_8H_{15}O_3N_3$  requires N = 21.02 per cent.).

*n-Butyl ether of isonitrosomalondimethylamide* (colourless form),  $(MeHN\cdot CO)_2C(NOC_4H_9)$ , is readily soluble in the cold in water and in all the ordinary organic solvents except ether in which it is only sparingly soluble, and separates in well-formed, rhombic prisms melting at 66° (Found: N = 20.09.  $C_9H_{17}O_3N_3$  requires N = 19.80 per cent.).

### III.—*Preparation of the Ethers of isoNitrosomalondibenzylamide by the Action of the Alkyl Iodide in the Presence of Silver Oxide.*

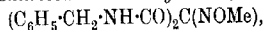
Only the methyl and ethyl ethers in this series were prepared, and the method was the same as that adopted in the case of the *isonitrosomalondimethylamide* series. The ethers, being soluble in benzene, were obtained by evaporation of the benzene solution after filtering from the silver iodide and excess of oxide.\* The

\* The silver residues were found to contain an appreciable amount of silver cyanide. Complete analysis of the residues gave the following results.  $Ag_2O = 47.5$ ;  $AgI = 45$ ;  $AgCN = 7.5$  per cent.



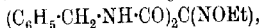
ethers are colourless, crystalline compounds, and therefore probably derivatives of the isooxime series,  $(C_6H_5 \cdot CH_2 \cdot NH \cdot CO)_2C \begin{smallmatrix} \nearrow NR \\ \searrow O \end{smallmatrix}$ .

*Methyl ether of isonitrosomalondibenzylamide,*



is readily soluble in alcohol or benzene, sparingly soluble in amyl alcohol, and insoluble in water or light petroleum. It crystallises from a mixture of amyl alcohol and petroleum (b. p. 40–60°) in slender, acicular prisms melting at 83.5° (Found: N = 12.9,  $C_{18}H_{19}O_3N_3$  requires N = 12.92 per cent.).

*Ethyl ether of isonitrosomalondibenzylamide,*



is readily soluble in alcohol, ether, or benzene, less readily soluble in amyl alcohol, and insoluble in water. It crystallises in very small, colourless prisms from petroleum (b. p. 100–120°), and melts at 73.5° (Found: N = 12.36.  $C_{19}H_{21}O_3N_3$  requires N = 12.4 per cent.).

#### IV.—Methylation of isoNitrosomalonanilide by Means of Diazo-methane.

*Methyl Ether of isoNitrosomalonanilide* (yellow form),  $(PhHN \cdot CO)_2C:N \cdot OMe$ .—1. *isoNitrosomalonanilide* (1.4 grams), suspended in 15 c.c. of dry ether, was treated with a solution of diazo-methane in ether prepared from 3 grams of nitrosomethylurethane. There was a vigorous action, and a bulky, yellow solid separated; this was filtered after twelve hours and dried on porous earthenware. It was found to be the pure yellow *methyl ether of isonitrosomalonanilide*; it melts at 144° and decomposes at 150° (Found: N = 14.2.  $C_{16}H_{15}O_3N_3$  requires N = 14.14 per cent.). It is readily soluble in all the ordinary organic solvents, with partial conversion into the colourless isomeride. Repeated crystallisation from ethyl alcohol converts it completely into this isomeride, m. p. 194°.

2. Two grams of *isonitrosomalonanilide* (either the yellow or the colourless form) and 1 gram of nitrosomethylurethane were dissolved in 15 c.c. of absolute alcohol that had been dried with diazo-methane; 10 c.c. of a 2.3 per cent. solution of sodium ethoxide in absolute alcohol were then added gradually. There was a vigorous reaction, which was moderated by external cooling, nitrogen was evolved, and a solid separated. This was filtered after twelve hours, washed with water to remove the sodium cyanate, and found to consist of a mixture of the yellow and colourless methyl ethers of *isonitrosomalonanilide*. A further quantity was obtained from the alcoholic filtrate on addition of water. The two ethers could not be separated by crystallisation, and repeated crystallisation from alcohol yielded the pure colourless ether, m. p. 194°.

V.—*Methylation of isoNitrosomalonanilide by Means of Methyl Sulphate.*

Excess of methyl sulphate was added to an alcoholic solution of the pure potassium salt of isonitrosomalonanilide containing an aqueous solution of potassium carbonate. Methylation occurred at the ordinary temperature and was complete in a few hours. The product was the colourless methyl ether of isonitrosomalonanilide, m. p. 194°.

VI.—*Reduction of isoNitrosomalonanilide and its Ethers.*

isoNitrosomalonanilide or its methyl or ethyl ether is readily and quantitatively reduced to *aminomalonanilide*,  $(\text{PhHN}\cdot\text{CO})_2\text{CH}\cdot\text{NH}_2$ , by the action of (a) zinc dust and glacial acetic acid, (b) aluminium-mercury couple in moist ether or moist alcohol, (c) ammonium sulphide in alcoholic solution; the reduction being effected at the ordinary temperature. Aminomalonanilide crystallises from alcohol in brilliant, flattened prisms melting at 146° (Found: N = 15.68.  $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_3$  requires N = 15.6 per cent.).

In conclusion, we tender our thanks to the Department of Scientific and Industrial Research for a grant to one of us (A. G. R.) which has enabled this investigation to be carried out.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

SOUTH KENSINGTON, S.W.7.

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CCLIII.—*Adsorption and Catalysis in Fuller's Earth.*

By ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS.

IN the bleaching of edible oils by means of fuller's earth, it has frequently been noticed that the various types of earth employed, namely, Florida, Surrey, and Somerset, are not equally effective as colour-removing agents. This difference is not due to the variety of earth employed, since the order of efficiency in which the earths may be placed varies with the nature of the oil. Evidently there is some other factor to be considered in addition to the direct adsorption of the colouring matter. The extensive use of oxidising agents for palm-oil bleaching, which may be fat-soluble oxidants such as benzoyl peroxide, or fat-insoluble substances such as the dichromates, or air in the presence of fat-soluble catalysts as in the case of manganese oleate (compare Rai, *J. Soc. Chem. Ind.*, 1917, **36**, 948), indicates that some colour-removal during the treatment with the fuller's earth may in part

be due to a catalytic activity of the earth as an oxidising agent, the source of oxygen being the adsorbed air in the fresh material. It was considered of interest to investigate whether the catalytic properties of the various grades of earth were dependent on their adsorptive capacities, and how these in turn were related to their specific surfaces.

#### EXPERIMENTAL.

*Specific Surface.*—The relative specific surfaces of the sample of three varieties of fuller's earth derived from Florida, Surrey, and Somerset, respectively, were determined by means of an elutriator previously calibrated with standard barium sulphate.

One gram of each earth was fractionated in the elutriator, and the amounts driven over at different flow rates were collected, dried, and weighed. The relative specific areas of each fraction were calculated from the average of the mean diameters of a number of grains in each portion. The results obtained were as follow.

##### *Florida Earth.*

Head of water in mm.	Amount driven over.	Amount per cent.	Average diameter in mm.	Relative surface.	Total relative surface.
3	0.0950	9.50	0 — 0.092 = 0.046	206	576
5	0.1268	12.68	0.092 — 0.122 = 0.107	118	
7	0.1946	19.46	0.122 — 0.162 = 0.143	138	
Residue	0.5842	58.42	0.5	116	

##### *Surrey Earth.*

3	0.8230	82.30	—	1800	1874
5	0.0400	4.00	—	37	
7	0.0228	2.28	—	16	
Residue	0.1065	10.65	—	21	

##### *Somerset Earth.*

3	0.4403	44.03	—	957	1327
5	0.2165	21.65	—	202	
7	0.2000	20.00	—	140	
Residue	0.1432	14.32	—	28	

It is evident that there are marked differences in the relative specific surfaces, the order in decreasing fineness being Surrey, Somerset, and Florida, standing in the ratios 2.35 : 2.13 : 1, the last comparing unfavourably with the other two.

*Adsorptive Power.*—For the rapid attainment of equilibrium in adsorption it was necessary to select some material which not only exhibited marked positive adsorption, but at the same time did not have a high penetration coefficient. In investigating the

catalytic activity of the earths, the period of investigation was restricted to a few hours and the reaction was such that the micropores in the material were in all probability either filled with water or oxygen gas, the catalytic surface being confined to the exterior and the surface of the macropores. To obtain comparable values from experiments on adsorption, the material should be strongly adsorbed on the surface of the exterior and of the macropores, and penetrate but slowly, if at all, into the micropores; as substances most suitable to fulfil these conditions, malachite-green and methylene-blue were employed. It was found, however, that with the former the comparison of the intensities of colour in the tintometer could not be carried out with any high degree of accuracy. With methylene-blue, on the other hand, utilising a yellow filter for the illuminating beam, the green tints of the various dye solutions could be accurately compared with those of standard solutions of the dye. In each experiment, 200 c.c. of a solution of known concentration of the dye were agitated with 1 gram of earth, and the residual concentration after forty-eight hours' contact was determined with the aid of the tintometer. The following results were obtained :

Grams of dye in 200 c.c. of original solution.	Adsorbent.					
	Florida.		Surrey.		Somerset.	
	<i>x</i> .	<i>c</i> .	<i>x</i> .	<i>c</i> .	<i>x</i> .	<i>c</i> .
0.0818	0.044	0.037	all	traces	all	traces
0.1638	0.053	0.111	0.105	0.059	0.097	0.067
0.3276	0.067	0.261	0.146	0.182	0.112	0.216
0.5062	0.078	0.428	0.182	0.317	0.121	0.385
0.6492	0.084	0.566	0.223	0.426	0.125	0.524
0.9850	0.089	0.896	0.273	0.712	0.136	0.849
1.1248	0.091	0.034	0.283	0.941	0.139	0.986
1.2662	0.090	0.176	0.289	0.977	0.140	1.126

*x* = amount of dye adsorbed.

*c* = grams of dye in 200 c.c. of solution at equilibrium.

The earths thus differ very markedly in their adsorptive powers for methylene-blue, the Surrey earth being extremely effective and the Florida relatively poor. The order of the earths in adsorptive power is thus identical with the order of the specific surfaces as determined by the elutriator.

On plotting the values of  $\log x/c$  as a fraction of the adsorbed quantities, *x*, according to the adsorption isotherm of Williams (*Proc. Roy. Soc.*, 1919, [A], 96, 287), approximately linear relationships are obtained satisfying the following equations :

$$\begin{aligned} \text{Florida} \quad \log_{10} x/c &= 1.212 - 25.7x. \\ \text{Somerset} \quad \log_{10} x/c &= 2.524 - 24.5x. \\ \text{Surrey} \quad \log_{10} x/c &= 0.383 - 3.2x. \end{aligned}$$

Since the relative adsorption of the methylene-blue falls off with increasing concentration of the solution, the relative adsorptive powers for the different earths can be expressed in numerical form by solving the above equations for the case where the bulk concentration of the solution is equal to the amount adsorbed per gram of earth, that is,  $\log. x/c = 0$ .

The equilibrium concentrations for equipartition of the methylene-blue between solvent and adsorbent are as follow: Florida, 0.0471 gram per 200 c.c.; Somerset, 0.1030 gram per 200 c.c.; Surrey, 0.1197 gram per 200 c.c., giving a ratio of 1:2.18:2.54 closely parallel to the ratios of the specific surfaces.

Time in minutes.	Florida.		Surrey.		Somerset.	
	Volume of oxygen collected.	$k \times 10^5$ .	Volume of oxygen collected.	$k \times 10^5$ .	Volume of oxygen collected.	$k \times 10^5$ .
30	20.05	2.22	22.50	2.39	4.80	0.53
60	42.50	2.67	41.90	2.40	10.06	0.56
90	60.00	2.42	58.30	2.29	14.98	0.54
120	78.85	2.51	74.00	2.32	19.99	0.55
150	95.00	2.54	87.90	2.30	24.96	0.55
180	108.50	2.53	100.95	2.30	29.89	0.55
200	116.10	2.51	109.28	2.32	—	—
210	—	—	—	—	34.91	0.56
240	131.25	2.51	125.00	2.33	39.86	0.57
300	150.0	2.51	143.00	2.31	—	—
330	—	—	—	—	59.48	0.59
400	173.5	2.50	166.18	2.28	—	—
420	—	—	—	—	69.25	0.61
540	193.4	2.40	185.00	2.14	88.40	0.74
Mean	1.70 232	2.51 (excluding the first value.)		2.31		0.58

*Catalytic Properties.*—It was noted that fuller's earth exerted a catalytic action on the decomposition of hydrogen peroxide, and a comparison of the catalytic properties of the three varieties of earth was carried out with this material. The comparison was effected in the following manner.

Fifty c.c. of a solution of pure hydrogen peroxide (perhydrol) of strength 14.08 grams per litre (equivalent to 232 c.c. of oxygen) and 2 grams of the earth were kept in violent agitation by means of a stirrer rotating at the speed of 720 r.p.m. in a large boiling-tube immersed in a thermostat at  $24.4^\circ$ . The oxygen evolved was collected in a gas burette, the water-jacket being maintained at the same temperature as the thermostat by means of a water-circulation pump.

The reactants were neutral to litmus and a blank control yielded a negligible amount of oxygen (0.6 c.c. in 210 minutes). The

reaction velocity coefficients were calculated from the expression for a unimolecular surface reaction,  $dx/dt = k(a-x)$ , to the Napierian base and the second as unit of time. The observed rate of oxygen evolution and the values of the reaction velocity coefficients calculated from the smoothed curves are shown in the table on p. 2122.

Evidently, the catalytic effects are in no way related to the specific surface or to the adsorptive power for methylene-blue. With such a differentiation in properties, a possible explanation for the anomalous effects of the various earths on the bleaching of oils suggests itself—colour bleaching is in part due to adsorption and in part produced by catalytic oxidation.

Since the catalytic properties are independent of the surface extension, it seemed probable that there exists in the material some specific oxidation catalyst, in all probability iron. The analyses of the three earths gave the following results.

Earth.	Adsorbed water per cent.	Iron as $\text{Fe}_2\text{O}_3$ .
Florida .....	7.64	6.98
Surrey .....	14.25	6.40
Somerset .....	12.32	3.15

It will be noted that the adsorbed water runs closely parallel both to the specific surface and to the adsorption of methylene-blue, whilst the iron contents are in the same order as their catalytic activities, the ratios of the Surrey to the Florida (1:1.09) being identical with the ratio of the catalytic activities of these two earths. In the case of the Somerset earth the iron content is in excess of that anticipated from the catalytic activity, but it will be noted in this case that the velocity coefficient shows a continuous increase in value, indicating an increasing activity on the part of the iron.

#### *Summary.*

The three typical varieties of fuller's earth—Florida, Surrey, and Somerset—are widely different in specific surface, adsorption, and catalytic activities. The adsorption of methylene-blue from aqueous solutions is approximately proportional to the specific surfaces of the earths (neglecting porosity, if any), whilst the catalytic activities in the decomposition of hydrogen peroxide are not dependent on the adsorptive power. The iron content of the fuller's earth may be the governing factor in the catalysis.

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CCLIV.—*The Solubility of Phenanthrene in Various Organic Solvents.*

By HERBERT HENSTOCK.

IN connexion with some work on the bromination of phenanthrene, it was found necessary to obtain accurate data with respect to the solubility of the hydrocarbon in suitable solvents. So far, no very detailed measurements of this kind seem to have been made. Hildebrand, Ellefson, and Beebe (*J. Amer. Chem. Soc.*, 1917, **39**, 2301) describe experiments on the solubility of a number of compounds, one of which was phenanthrene, at 25°; in 100 grams of each of the following solvents the quantities of phenanthrene dissolved were: Ethyl alcohol, 4.91; benzene, 59.5; carbon disulphide, 80.3; carbon tetrachloride, 26.3; ethyl ether, 42.9; hexane, 9.15 grams. More particular determinations have now been carried out at temperatures between -10° and +30°.

The phenanthrene employed was recrystallised from ether in plates, melting at 101°, which were found to belong to the triclinic system (Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274r), and portions of this product were again crystallised from each solvent in which the solubility was to be determined, and were then dried at 25° for three or four hours. The following liquids are arranged in the order of their usefulness as crystallising media for phenanthrene: ether, light petroleum, ethyl alcohol, methyl alcohol, glacial acetic acid, acetone, carbon tetrachloride, chloroform, carbon disulphide, and benzene. Provided that the sample of phenanthrene is already fairly pure, it separates from ether in very pure, white, glistening crystals: the last four are all about equal as solvents, but they do not greatly improve the purity of the product. The density of phenanthrene is less than that of chloroform, carbon disulphide, or carbon tetrachloride, and greater than that of the other liquids.

All the solvents were purchased as chemically pure, but before use they were dried, over suitable desiccating agents, for three days and then distilled in bulk, the first and the last thirds of the volume being rejected, and the middle portion redistilled until a suitable fraction, having the correct boiling point, had been obtained. The ether was well washed with water before being subjected to the above treatment. Benzene and glacial acetic acid were frozen and the well-drained crystals remelted. The two alcohols were distilled over a little metallic sodium as a final precaution.

The apparatus employed was one similar to that used by Brönsted and Petersen (*J. Amer. Chem. Soc.*, 1921, **43**, 2265) in their work on the solubility of metal-ammonium salts. The modifications

TABLE I.  
Solubility of Phenanthrene.

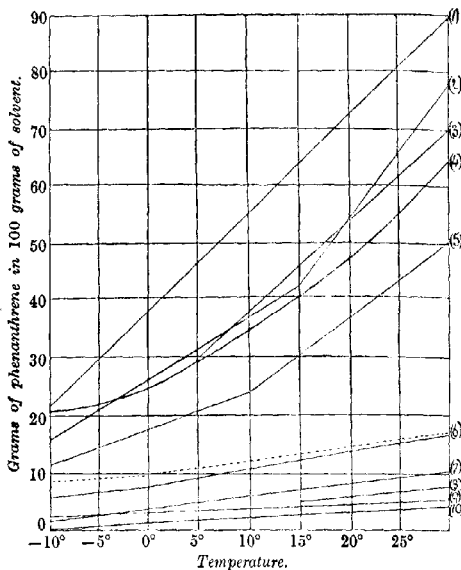
Solvents.	Temperatures.					
	-10°.	-5°.	0°.	5°.	10°.	15°.
Methyl alcohol .....	0	0.60	1.20	1.80	2.40	3.00
Light petroleum, b. p. 60-85° ...	0.8	1.60	2.40	3.20	4.00	5.00
Ethyl alcohol .....	1.75	2.25	2.75	3.26	3.77	4.28
Glacial acetic acid .....	—	—	—	—	—	5.00
Carbon tetrachloride .....	5.50	6.10	7.60	9.80	12.66	15.80
Ether .....	12.20	14.80	17.44	20.64	23.84	30.64
Acetone .....	15.70	20.00	25.50	31.02	36.54	42.50
Chloroform .....	21.20	22.70	25.50	29.60	34.30	39.90
Benzene .....	—	—	—	29.86	36.66	44.06
Carbon disulphide .....	21.60	28.84	37.32	45.88	54.48	63.28
	20°.	25°.	30°.	35°.	40°.	
Methyl alcohol .....	3.60	4.20	4.80			
Light petroleum, b. p. 60-85° ...	6.60	8.40	10.60			
Ethyl alcohol .....	4.80	5.50	5.81			
Glacial acetic acid .....	5.80	6.60	7.80	9.20	11.20	
Carbon tetrachloride .....	19.00	22.50	26.20			
Ether .....	36.78	43.22	50.42			
Acetone .....	51.84	63.50	77.48			
Chloroform .....	46.60	54.60	64.20			
Benzene .....	51.70	60.32	69.68			
Carbon disulphide .....	72.08	80.92	89.82			

introduced were an extra paddle on the stirring rod and, in the top of the tube, a rubber stopper having a hole through the centre, into which a piece of glass tube, of the same length as the stopper, was fixed as a bearing for the stirring rod; this was lubricated with a little glycerol. The stopper, which could be raised or lowered on the rod, to permit the introduction of solute or the removal of solution, was also bored with a side hole, which carried a thermometer reading to 0.1°; a similar thermometer was placed in the thermostat bath. At temperatures between -10° and 0°, freezing mixtures of ice and salt were used, from 0° to 10° a large volume of water, suitably cooled by ice, and above 10° a gas-regulated thermostat. From 0° upwards, the temperature could be kept constant to within 0.1° with very little trouble, but below 0° a single freezing mixture did not remain at a given temperature longer than about twelve or fifteen minutes; fresh mixtures were therefore made at this interval of time and the apparatus was transferred as rapidly as possible to the new mixture as soon as its temperature became constant. The only practicable method of determining the quantity of phenanthrene dissolved was found to be that of evaporating the solvent from a weighed amount of the solution and weighing the solid residue. A portion of the saturated solution was removed in a pipette, similar to that described by Chattaway and Lambert (T., 1915, 107, 1766), which was allowed to come to a temperature of 15° and weighed; the solvent



was evaporated slowly in a porcelain basin at  $25^{\circ}$ , the residue heated for fifteen minutes at  $60^{\circ}$ , allowed to cool, and weighed. In order to make sure that no phenanthrene was lost by this method, a further quantity of solvent was added to the solid, and its solution effected: on repetition of the evaporation and subsequent heating, no loss or discoloration was noticed.

FIG. 1.



(1) Carbon disulphide; (2) Acetone; (3) Benzene; (4) Chloroform; (5) Ether; (6) Carbon tetrachloride; (7) Light petroleum; (8) Glacial acetic acid; (9) Ethyl alcohol; (10) Methyl alcohol.

In preliminary experiments with each solvent, the time of stirring necessary to ensure saturation at temperatures up to  $0^{\circ}$  was found to be about two hours; between  $0^{\circ}$  and  $15^{\circ}$ , the time was about one and a half hours, and above  $15^{\circ}$  an hour sufficed: carbon disulphide, chloroform, benzene, and acetone required about half an hour extra in each case to become saturated.

Table I gives the solubility in grams of phenanthrene in 100 grams of each of the various solvents at the temperatures indicated.

These numbers represent the mean of three experiments at each temperature; the deviation of single experimental results from these figures at the lower temperatures was not more than  $0.2$  gram and at higher ones not more than about  $0.5$  gram.

These results are plotted in Fig. 1.

The solubilities at 25° in those solvents mentioned by Hildebrand, Ellefson, and Beebe (*loc. cit.*) are in fair agreement with their numbers, excepting in the case of carbon tetrachloride, for which the number was about 14.5 per cent. less than theirs. This discrepancy is much too great to be explicable by any of the ordinary errors of experiment. The whole of the work with this solvent was therefore carefully repeated with fresh solvent and solute, without, however, any radical alteration in the numbers obtained; but in order to check the method, a different one was devised and carried out. The procedure adopted was to heat 100 grams of the solvent to 10° above the temperature at which the solubility was required, and to make an almost saturated solution, weighing the quantity of phenanthrene dissolved, and then to cool the solution by 10° and keep it in a thermostat at that temperature for two to four hours: part of the solute crystallised out and was rapidly filtered off by suction through a funnel previously brought to the temperature of the solution. After complete drying, the weight of this solid was subtracted from the total quantity of solute used. Two complete determinations were made at each 5° between + 30° and - 10°; the mean of the results is shown in Table II.

TABLE II.

Grams of phenanthrene held in solution.		Grams of phenanthrene held in solution.	
Temperature.		Temperature.	
30°	26.42	5°	12.30
25	23.50	0	9.70
20	20.45	-5	8.80
15	17.40	-10	8.00
10	15.10		

The broken curve (6) in Fig. 1 shows the relationship of these figures to those obtained by the direct method. At 30°, the two meet, but below that temperature there is steadily increasing divergence. This *modus operandi* was also employed with the other solvents, but in some cases the rapid evaporation of the liquid during filtration coupled with the large quantity of the solute prevented the acquisition of accurate results. Those examined showed no regular divergent curves; some of the numbers for ethyl alcohol are:

Temperature .....	30°	25°	20°	15°	10°
Grams of phenanthrene held in solution .	5.90	5.25	4.82	4.20	3.75

They are in close agreement with those given by the first method (see Table I). This peculiarity of carbon tetrachloride is as yet unexplained.

Peddle and Turner (T., 1913, 103, 1202) show that the degree of association of salts in solution is one of the factors governing

solubility; they also state that a solvent like ethyl alcohol permits neither marked association nor ionisation. Since phenanthrene is not an ionisable substance, especially in saturated solution, it is evident from a consideration of Table I that the condition of the hydrocarbon, in solution in methyl or ethyl alcohol, light petroleum, or glacial acetic acid, must be almost normal, with little or no association amongst its molecules, especially when the low and great regularity of solubility is examined. Association in the remaining solvents must be much greater than in the preceding cases, approaching more nearly to that of the solvent as the temperature rises. For each solvent, with the possible exception of chloroform, there should be a temperature, below  $-10^{\circ}$ , at which phenanthrene becomes insoluble; this was reached only with methyl alcohol at  $-10^{\circ}$ . Chloroform is an anomalous substance with respect to solubility (see Peddle and Turner, *loc. cit.*).

The relationship between observed solubility and molecular percentage solubility, calculated on  $100n/N$ , where  $n$  and  $N$  = molecules of solute and solvent, respectively, is well defined in the first three liquids; the figures for methyl alcohol are typical.

Temperature	$-10^{\circ}$	$-5^{\circ}$	$0^{\circ}$	$5^{\circ}$	$10^{\circ}$	$15^{\circ}$	$20^{\circ}$	$25^{\circ}$	$30^{\circ}$
Mol. per cent.	0	0.106	0.217	0.325	0.435	0.550	0.653	0.761	0.871
Difference ...		0.106	0.111	0.112	0.110	0.115	0.103	0.108	0.110

(See Table I for observed solubilities.)

The difference is a constant quantity in both cases. The figures for the remaining solvents show a similar relationship, but the values increase with rise of temperature.

The curves (Fig. 1) for carbon tetrachloride, ether, and acetone show marked breaks at  $0^{\circ}$ ,  $10^{\circ}$ , and  $15^{\circ}$ , respectively, which point to some change in the solvents or solutes at those temperatures, and in this connexion Turner (T., 1911, 99, 880) states that miscibility of two substances is possible when both are normal or both associated, but that solubility is limited when one substance is normal and the other associated. The points referred to, therefore, probably indicate a sudden alteration in the association of the molecules of phenanthrene, which will tend to bring the molecular association of solvent and solute nearer together, causing a sharp rise in solubility.

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CLV.—*The Isomerism of Metallic Oxides. Part I.*  
*Lead Monoxide.*

By MALCOLM PERCIVAL APPLEBEY and ROBERT DOUGLAS REID.

LEAD MONOXIDE occurs naturally in two crystalline forms, litharge and massicot, which are yellow and red, respectively. These can also be obtained in the laboratory by artificial means. It has been long known that the red form can be converted into the yellow by heating and the yellow into the red by long-continued action of light at the ordinary temperature. The difference between the two forms has been attributed by many investigators to polymorphism, the red being regarded as the more stable form at the ordinary temperature and at all temperatures up to a transition point which has not been precisely determined. This explanation is supported by the difference of density of the two forms observed by Geuther (*Annalen*, 1883, **219**, 56) and by Ruer (*Z. anorg. chem.*, 1906, **50**, 265), whose observations agree in ascribing the lower density to the red form, although their actual values are somewhat widely divergent (Geuther, red 9.13, yellow 9.29; Ruer, red 9.37, yellow 9.52). Ruer also determined by a conductivity method the solubility of the two forms in water, which he found to be  $1.00 \times 10^{-4}$  gram-equiv. per litre for the yellow form and  $0.56 \times 10^{-4}$  for the more stable red form. Solubilities determined by the conductivity method for substances like litharge are not very trustworthy, but the values for the two forms probably give a fairly correct idea of the relative solubility.

The crystallographic evidence also points to polymorphism. Nordenskiöld (*Pogg. Ann.*, 1861, **114**, 619) determined the form of the yellow modification to be rhombic bipyramidal and that of the red to be tetragonal. Larsen (*U.S.A. Geol. Survey Bull.*, 1921, **679**, 105), working both with mineral forms and with laboratory products, confirmed Nordenskiöld's conclusions, and found, moreover, that the yellow form is always biaxial and positive in its action on polarised light, whilst the red is uniaxial and negative.

The explanation of these differences as due to polymorphism has recently been attacked by Glasstone (*T.*, 1921, **119**, 1689, 1914). Using preparations of lead monoxide obtained by the action of alkalis of various strengths on solutions of lead salts, he has found, both by gravimetric and electrometric measurements, approximately identical solubility for lead oxide preparations irrespective of their colour, and has drawn the conclusion that the differences of colour are due, not to polymorphic change, but to variations of the state of division of the substance. The change of red to yellow on heating is attributed to formation of larger agglomerates, which on rubbing will

break down again into a reddish-brown powder, consisting of particles rather smaller than the original red form. The crystallographic evidence is regarded as indecisive and that from density and from solubility, determined by conductivity, is rejected for the reasons stated above.

Methods for the preparation of both the red and the yellow varieties in the form of definite crystals of fair size had already been worked out in this laboratory, and experiments on their solubility relations were being developed at the time when Glasstone's papers appeared. It was therefore at once apparent to us that Glasstone's theory could not be correct. Any differences of property which could be measured could not be due to differences in the state of division when both forms could be obtained in plainly visible crystals. There seemed also an inherent improbability in the view that the change from yellow to red could be effected by light if the change simply consisted in alteration of the size of particle. This argument has also been brought forward by Baly (*Ann. Reports*, 1921). We have, however, thought it advisable to carry out solubility measurements both by gravimetric and electrometric methods with the crystalline oxides, following Glasstone's procedure in every detail, before expressing ourselves as satisfied with the polymorphism theory. These determinations have now definitely shown that the two forms have widely differing solubilities and are perfectly distinct and different. We have drawn the conclusion that the results obtained by Glasstone are possibly due to the fact that none of his methods of preparation gave a pure red oxide, with the result that all his solubility determinations gave values approximating to the solubility of the yellow form which was present.

#### *Methods of Preparation.*

The methods used in the preparation of crystalline lead monoxide are based upon experiments made by Lambert in the course of his researches on the corrosion of lead (T., 1915, 107, 210). We are greatly indebted to him for much information and advice in carrying out the preparations, and also for providing us with a specimen of his purest redistilled lead, which we have used as an electrode in the electrometric measurements to be referred to later. The method consists in the dehydration of Kahlbaum's purest lead hydroxide by digestion with strong potassium hydroxide solution at temperatures approaching the boiling point. The operation is performed in a small flask fitted with an air-condenser, at the upper end of which is a soda-lime tube to prevent the formation of carbonate. The hydroxide goes into solution in considerable quantity when the temperature is raised, and, on slowly cooling, the oxide is deposited

in a well-crystallised form. Which form is obtained depends on the concentration of the alkali, high concentrations giving the red form, moderate concentrations the yellow, and low concentrations apparently a black or steel-grey variety which is similar in form to the yellow oxide and has not yet been subjected to detailed investigation. The rate of cooling is also not without effect on the product, rapid cooling favouring the yellow form. The following table summarises these observations.

TABLE I.  
Preparation of lead monoxide.

Normality of KOH.	Colour.	Crystalline form.
15	Red	Square plates. Tetragonal, uniaxial, -ve.
10	Mixtures of red and yellow Yellow	Needle-like, rhombic, bipyramidal, biaxial, +ve.
3	Varying shades of green Steel-black	" "

The red crystals produced by this method show a beautiful iridescence when in contact with their mother-liquor. If the conditions are carefully adjusted, microscopic examination shows no trace of the lemon-yellow needles. When shaken up with water, the solution is quite clear and gives no indication of the existence of ultramicroscopic particles. There can therefore be little doubt that we are here dealing with a pure substance. Both the red and the yellow forms were analysed for peroxide content and showed only a negligible quantity (0.67 per cent. in the yellow and 0.63 per cent. in the red).

With regard to the black form, the appearance of which certainly suggests either lead suboxide or metallic lead, we are not in a position to make any definite statement. It may be a third variety of the oxide, or it may possibly be a yellow form which has in some way suffered superficial reduction. We record, however, an interesting observation we have made as to the action of sunlight on the yellow needle form. Two samples were exposed to light for a period of nine months, the one in a vacuum and the other in a tube exposed to the air. Both were largely transformed into the steel-grey and not into the red form, whilst identity of behaviour showed that atmospheric oxygen could have played no part in the change. A similar blackening has been observed by Renz (*Z. anorg. Chem.*, 1921, **116**, 62), and is attributed by him to the photochemical dissociation of the oxide and the formation of metallic lead.

Mr. T. V. Barker has kindly made a microscopic examination of the red and yellow modifications and reports:—"The colour of the

first is extremely variable, passing from red through brown to light yellow. It crystallises in square plates which exhibit a negative uniaxial figure in convergent light, and the system is therefore presumably tetragonal. The second modification, which is uniformly yellow when freshly prepared, crystallises in elongated, strongly doubly refracting plates with straight extinction. The ray vibrating parallel to the direction of elongation has the greater refractive index, so that even if the system be tetragonal (which is in doubt) the sign of the double refraction is positive. The two forms, then, exhibit distinctly different optical properties and must be held to present a true case of dimorphism."

We have determined the densities of the red and yellow oxides, taking care to remove all traces of occluded air in a vacuum desiccator. The values, 9.27 for the red and 8.70 for the yellow, are quite distinct, although, strange to say, the difference is in the opposite direction to that observed by Geuther and Ruer (*loc. cit.*).

If the yellow crystalline form is ground in a mortar, a brownish-red powder is obtained. The change of colour, attributed by Glaston to fineness of division, is, in our view, to be explained as a change to the red, stable form, analogous to the change of the unstable yellow form of mercuric iodide to the stable red form under similar treatment.

If the black form of oxide is ground, it first becomes yellow and then reddish-brown. On further violent grinding, streaks of bright red are plainly visible under the pestle, but it seems impossible, probably owing to mechanical difficulties, to reduce the whole mass to this condition. If, however, the finely ground material is shaken in a tube with water and allowed to settle, the deposit shows an interesting gradation of colour from black at the bottom to scarlet at the top. The red form is here, then, undoubtedly the ultimate product of grinding and has the smallest particle. Every investigator so far has shown it to be the least soluble, a fact which does not support any theory connecting the solubility with size of particle.

#### *Solubility Determinations.*

*Gravimetric Method.*—The solubility of the two forms was measured in solutions of sodium hydroxide prepared according to the method of Ming Chow (*J. Amer. Chem. Soc.*, 1920, **42**, 458) and was standardised with hydrochloric acid of constant boiling point. It was found that during the electrolysis of sodium hydroxide solution, in the former preparation, the temperature had to be kept below about 60°, otherwise black "mercurous oxide" was formed. The solutions were placed in contact with pure well-crystallised specimens of the oxide and stirred by a slow current of purified air as recommended

by Glasstone in order to avoid the abnormalities due to fracture of crystals which easily occur with more violent agitation. The results in Table II show that, in the case of the red form, no supersaturation effect is observed and the solubility rises towards a constant maximum. With the yellow form, there is initial supersaturation due to fineness of particle. It is clear, however, from the results that final equilibrium is only obtained by such methods after a very considerable time. Further experiments of much longer duration are shown in Table III. In these experiments there was no continuous stirring, but the containing tubes were inverted each day. The solutions were analysed by precipitation of the lead with sulphuric acid, the solubility of the lead sulphate being reduced by the addition of as much alcohol as could safely be used without throwing out sodium sulphate, which is very sparingly soluble in strongly alcoholic solutions.

It was found that alcohol to the extent of 25 per cent. of the final mother-liquor could be safely employed; the amount of lead unprecipitated being then very slight.

TABLE II.

Solubility of lead monoxide in *N*-sodium hydroxide with stirring by slow air-stream at 20.0°.

Form.	Time (days).	Conc. (Gram-mol./litre).	Form.	Time (days).	Conc. (Gram-mol./litre).
Red	3	0.0104	Yellow	3	0.0344
	5	0.0116		7	0.0289
	8	0.0126			
	11	0.0132		3	0.0359
	2	0.0088		8	0.0263
	2	0.0085			
	4	0.0099			
	6	0.0105			

TABLE III.

Solubility of lead monoxide in *N*-sodium hydroxide, without stirring, at 20.0°.

Form.	Time (days).	Conc. (Gram-mol./litre).	Form.	Time (days).	Conc. (Gram-mol./litre).
Red	4	0.0185	Yellow	5	0.0376
	7	0.0149		7	0.0334
	10	0.0165		9	0.0342
	5 months	0.0138		5 months	0.0240
	"	0.0136		"	0.0233
	"	0.0145		"	0.0239
Mean final value for the yellow oxide in <i>N</i> -NaOH 0.0237 gram-mol./litre.					
"	"	" red	"	"	0.0140

These experiments show definitely that the yellow form is nearly twice as soluble in *N*-sodium hydroxide as the red form, the actual



ratio (1.7:1) agreeing well with the ratio of the solubilities in water (1.8:1) determined by Ruer (*loc. cit.*).

*Electrometric Method.*—These were made by means of a Gambrell potentiometer reading to 0.0001 volt. It was calibrated against resistance boxes correct to 1 in 20,000. A cadmium cell was made in the usual manner and compared with a standard cell made by Gambrell. For the lead electrode the pure metal was melted under hydrogen, and a previously prepared platinum electrode dipped in it while in the molten state. The subsequent procedure was identical with that recommended by Glasstone. The standard alkali electrode described by Donnan and Allmand (T., 1911, 99, 845) was used to complete the cell. Throughout the experiments the electrodes were tested against three freshly prepared calomel electrodes, and any deviation from the value given by the authors was introduced as a correction. We have therefore some record of the working of this standard cell over a considerable period and the results are not without interest. The type of vessel used was exactly as described, with a three-way tap.

The mercuric oxide was prepared by heating Kahlbaum's pure mercuric nitrate. The cells in all *E.M.F.* experiments were placed in a thermostat kept at 20° within 0.05°.

TABLE IV.

*E.M.F.* of cell Hg/HgCl in KCl solution/HgO in NaOH solution/Hg.

Age (days).	<i>E.M.F.</i> (volt).	Donnan and Allmand's value.	Normality of electro- lytes.	Age (days).	<i>E.M.F.</i> (volt).	Donnan and Allmand's value.	Normality of electro- lytes.
1.2	0.1504	0.1504	1.00	9.5	0.1505	0.1504	1.00
9.1	0.1507			13.8	0.1505		
				47.0	0.1503		
* 0.4	0.1391			* 0.7	0.1397	0.1479	0.10
3.5	0.1393			1.6	0.1398		
17.0	0.1398						
				0.1	0.1472		
0.6	0.1500			4.9	0.1474		
4.0	0.1501			8.7	0.1474		
6.6	0.1502						

It will be seen from Table IV that the electrode behaved very well and can evidently be kept for very long periods without suffering appreciable change. In the two cells shown by an asterisk, however, the value is very much lower than normal; this was found to be due to the fact that a little undecomposed nitrate was present in the mercuric oxide. It is evident that this source of error must be carefully guarded against in setting up the standard alkali electrode. Table V shows the readings obtained with a cell where the liquid was stirred by an air-current. The process of solution, although

irregular, shows no tendency to exhibit supersaturation, the *E.M.F.* slowly decreasing and the solubility therefore increasing. Bubbling was in all cases stopped some time before making the reading in order to avoid any oxygen electrode effect.

TABLE V.

*E.M.F.* of cell Hg/HgO in *N*-NaOH/Red PbO in *N*-NaOH/Pb, with stirring.

Age (days).	<i>E.M.F.</i>	Age (days).	<i>E.M.F.</i>
0	0.6920	8	0.6859
1	0.6885	10	0.6868
2	0.6876	13	0.6847
3	0.6873	14	0.6827
4	0.6864	15	0.6828
6	0.6851		

Without stirring, approximately constant minimum values of *E.M.F.* for the red oxide, 0.6758, 0.6755, 0.6768 volt, were obtained at from four to seven days. These correspond with a state of supersaturation, after which the *E.M.F.* steadily increases over a long period to its constant value. As with the gravimetric experiments, the solutions were left for five months at 20° in contact with the solid, after which, on being placed in the cells, they gave definite values for the *E.M.F.* in the course of several days.

TABLE VI.

*E.M.F.*'s of cells Pb/PbO in *N*-NaOH/HgO in *N*-NaOH/Hg with five months' old solution of PbO in *N*-NaOH, without stirring.

Yellow form.	Red form.
0.6735	0.6807
0.6735	0.6806
0.6734	0.6810
0.6735	0.6806
0.6733	0.6808
	0.6811
Mean 0.6734	Mean 0.6808

The difference between the ultimate solubilities of red and yellow forms is represented by an *E.M.F.* of 0.0074 volt. The difference which would be predicted from the gravimetric solubilities, namely, 0.0140 and 0.0237 gram-mol. per litre, by the expression  $RT/nF \cdot \log c/c'$  is 0.0066 volt.

The ratio of solubilities of the yellow and red forms by the electrometric method is thus in good agreement with the gravimetric determinations.

Table VII shows some of the more important constants which can be derived from the measurements made. A column of Glasstone's results for what he regards as the single oxide is added for com-

parison. He worked at 25°, and corrections have been introduced according to the temperature coefficient which he gives. It will be seen that his values for the first three quantities (dependent on each other) fall between those we have obtained for the two forms. They approximate to the values for the more soluble or yellow form, as might be expected were he dealing with a mixture. The evaluation of the dissociation constant for the amphoteric plumbous hydroxide, as an acid, involves a knowledge of the solubility of lead monoxide in water. Ruer, from his conductivity measurements, gives the two values,  $0.50 \times 10^{-4}$  and  $0.28 \times 10^{-4}$  gram-mol. per litre, which have been used in our calculations. Pleissner (*Arch. Kaiser. Gesundh.*, 1907, **26**, 384) gives a whole series of values, by the same method, varying from  $0.077 \times 10^{-3}$  to  $0.403 \times 10^{-3}$ . He does not differentiate at all clearly between the two forms, and it seems fairly certain that he was dealing with mixtures. Glasstone uses one of the values,  $0.26 \times 10^{-3}$ , for his calculation.

TABLE VII.  
Various constants at 20°.

	Red form.	Yellow form.	Glasstone's form.
E.M.F. of electrode Pb/PbO in N-NaOH, volts.	0.5668	0.5594	0.562
Pb <sup>++</sup> conc. in N-NaOH, gram-ion per litre.	$0.90 \times 10^{-15}$	$1.80 \times 10^{-15}$	$1.6 \times 10^{-15}$
Solubility product $[Pb^{++}][OH']^2$	$0.47 \times 10^{-15}$	$0.91 \times 10^{-15}$	$0.82 \times 10^{-15}$
Dissociation constant of $Pb(OH)_2$ as an acid.	$0.33 \times 10^{-11}$	$0.39 \times 10^{-11}$	$1.3 \times 10^{-11}$

#### Summary.

1. The necessary conditions for preparing the yellow and red varieties of lead monoxide in well-crystallised forms have been explored.

2. The solubilities of the two forms in N-sodium hydroxide have been measured both gravimetrically and electrometrically. The solubility of the yellow form at 20° is about 1.8 that of the red form.

3. The evidence from solubility and from examination of crystalline form shows clearly that the yellow and red forms are polymorphic modifications.

4. The standard alkali electrode, Hg/HgO in N-NaOH, has shown itself to be easily reproduced and constant over long periods.

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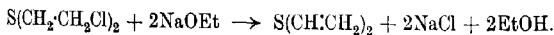
CCLVI.—*Hydrolysis of  $\beta\beta'$ -Dichlorodiethyl Sulphide.  
Synthesis of Divinyl Sulphide and the Preparation  
of a Non-vesicant Isomeride of  $\beta\beta'$ -Dichlorodiethyl  
Sulphide.*

By SIDNEY HARTLEY BALES and STANLEY ARTHUR  
NICKELSON.

DURING an investigation on the behaviour on keeping of impure  $\beta\beta'$ -dichlorodiethyl sulphide, prepared by the sulphur chloride-ethylene process, it was found necessary to study the hydrolysis of the purified substance.

After hydrolysis with 20 per cent. alcoholic potassium hydroxide, it was found that the product had a pronounced odour of garlic and that, on distilling off the alcohol, the odour was confined to the distillate, the residue being practically odourless. On pouring the alcoholic distillate into water, a clear, colourless, light oil separated. After thorough washing with water and drying over calcium chloride, the yield of oil was about 26 per cent. of the weight of  $\beta\beta'$ -dichlorodiethyl sulphide taken. Using 20 per cent. alcoholic potassium hydroxide, the same yield was repeatedly obtained. The liquid was found to distil very largely at  $83-87^\circ$ . Further fractionated, the bulk of the liquid distilled at  $85-86^\circ$  and had  $d_4^{20}$  0.9174. On keeping in stoppered glass vessels, the liquid polymerised in upwards of forty-eight hours to an opaque jelly, somewhat soluble in boiling carbon disulphide, but insoluble in alcohol, ether, benzene, carbon tetrachloride, or chloroform.

Helfrich and Emmet Reid (*J. Amer. Chem. Soc.*, 1920, 42, 1219) state that when  $\beta\beta'$ -dichlorodiethyl sulphide is acted on with sodium ethoxide, the product is not *s*-diethoxydiethyl sulphide, as they anticipated, but an easily polymerisable liquid which they surmised might be divinyl sulphide, thus:—



Furthermore, they state (*loc. cit.*) that on hydrolysis of  $\beta\beta'$ -dichlorodiethyl sulphide with caustic alkali in 50 per cent. alcohol, a small quantity of a heavy oil is obtained which they surmise might be a polymeride of divinyl sulphide. In neither case, however, was the investigation pursued further.

This observation has been confirmed by us, and the heavy oil (yield about 2.5 per cent. of the weight of  $\beta\beta'$ -dichlorodiethyl sulphide taken) is under investigation. In these circumstances (hydrolysis with 20 per cent. sodium hydroxide in 50/50 alcohol-water), no light oil was obtained.

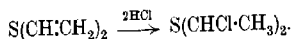
According to Beilstein and Richter, divinyl sulphide boils at  $101^\circ$  and has  $d$  0.9125. The only authority for these constants that could be found was Semmler (*Annalen*, 1887, **241**, 92), who describes the properties of divinyl sulphide which he obtained from natural sources (*Allium ursinum*). The density given is in fair agreement with that obtained for the product of hydrolysis of  $\beta\beta'$ -dichlorodiethyl sulphide above, but there is wide discrepancy in the boiling points obtained.

Concentrated nitric acid acts upon the liquid (as upon the polymeride) with extreme violence (Found: S = 36.84, 37.15.  $C_4H_6S$  requires S = 37.23 per cent.).

Vapour density determinations (V. Meyer) on the freshly distilled liquid gave molecular weight results which were in substantial agreement with the theoretical value for divinyl sulphide. Actually these results were 2–3 per cent. higher than the theoretical (86.1). This is no doubt due to slight polymerisation of the liquid during the experiment.

*A Non-vesicant Isomeride of  $\beta\beta'$ -Dichlorodiethyl Sulphide.*

Divinyl sulphide should add on two molecules of hydrogen chloride, giving a dichlorodiethyl sulphide, probably the  $\alpha\alpha'$ -compound:



Boiled with concentrated hydrochloric acid under reflux, the liquid under discussion blackens and apparently complete decomposition follows. When dry hydrogen chloride, however, is passed into the liquid (distilling at  $83$ – $87^\circ$ ), the gas is absorbed quietly and readily without appreciable evolution of heat. It is sufficient that the absorption vessel be immersed in cold water. Twenty-five grams of liquid absorbed 19 grams of hydrogen chloride in about five hours, that is, an absorption of about 90 per cent. of the theoretical. Owing to the slowing down of the rate, no attempt was made to obtain theoretical absorption. The liquid thus obtained was distilled under reduced pressure. A clear, colourless liquid having a most pungent, objectionable, and persistent odour and distilling at  $58$ – $61^\circ/15$  mm. was obtained. The yield from 25 grams was 35 grams, that is, about 75 per cent. of the theoretical. By careful redistillation, a product was obtained, b. p.  $58.5$ – $59.5^\circ/15$  mm.,  $d_4^{20}$  1.1972.

From the smoothness and ease with which the hydrogen chloride was absorbed, it would seem highly probable that simple addition occurred, whilst the sharpness of boiling point of the product, which was repeatedly obtained, indicates that the product is a simple substance.

The additive compound reacts violently with nitric acid. The chlorine is readily removed by alcoholic alkali (Found : S = 20.06, 20.18; Cl = 44.20, 44.22.  $C_4H_8Cl_2S$  requires S = 20.16; Cl = 44.60 per cent.). This substance, which appears to be devoid of vesicant properties, no precautions being taken while handling it without any discomfort being experienced, decomposes on distillation at atmospheric pressure with the evolution of copious fumes of hydrogen chloride, liquid distilling between  $120^\circ$  and  $145^\circ$ .

Further work on the hydrolysis of  $\beta\beta'$ -dichlorodiethyl sulphide and on the properties and reactions of divinyl sulphide, particularly with regard to the action of halogens and halogen acids, is in progress.

The authors wish to express their thanks to the Director of Artillery for permission to publish this note, and to the Director of Chemical Inspection, Mr. G. H. Perry, O.B.E., B.Sc., F.I.C., for the critical interest he has taken in the work.

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## CCLVII.—*Monothioethylene Glycol.*

By GEORGE MACDONALD BENNETT.

A MORE detailed study has now been made of the physical and chemical properties of monothioethylene glycol, the isolation of which was recently recorded (T., 1921, **119**, 422). It had been prepared in a very impure condition by Carius (*Annalen*, 1862, **124**, 257), who stated that it was not completely miscible with water and that when heated at  $100^\circ$  it was decomposed with evolution of hydrogen sulphide. The substance is actually completely miscible with water, and when in a state of purity, in particular of freedom from all trace of mineral acid, it may be distilled almost without decomposition at the ordinary pressure; the vapour density, determined under a pressure of half an atmosphere at  $158^\circ$ , is normal.

The mercaptides of a series of metals with monothioethylene glycol have been prepared. They are remarkable for their low melting points and ready solubility in warm water and a number of organic solvents.

Decomposition of the hydroxy-mercaptan in the manner described by Carius does not occur under any conditions. On the other hand, in the presence of mineral acids decomposition occurs more or less rapidly according to the temperature, with production of white polymeric ethylene sulphide of high molecular weight similar in

properties to the substances described by Löwig and Weidmann (*Annalen*, 1840, **36**, 321) and Mansfeld (*Ber.*, 1886, **19**, 696). Dilute hydrochloric acid induces this decomposition, the mechanism of the action in this case being indicated by the fact that hot concentrated hydrochloric acid converts monothioethylene glycol in a few seconds into the corresponding  $\beta$ -chloroethyl mercaptan,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SH}$ . This is an unstable substance which decomposes readily in the moist condition with production of white polymeric ethylene sulphide. It is decomposed by prolonged washing with cold water, but when dry it may be distilled undecomposed at the ordinary pressure. It shows the high degree of chemical and physiological activity characteristic of the simple  $\beta$ -chloroethyl sulphur derivatives.

In the ease with which the hydroxyl group of monothioethylene glycol is replaced by chlorine by the action of hot fuming hydrochloric acid, it shows a close resemblance to  $\beta\beta'$ -dihydroxydiethyl mono- and di-sulphides, the properties of the hydroxyl group in this respect being rather those of a tertiary than of a primary alcohol group.

A number of other derivatives of monothioethylene glycol are under investigation.

#### EXPERIMENTAL.

##### *Physical Constants of Monothioethylene Glycol.*

A slight modification was found desirable of the method of preparation of the mercaptan given previously (*loc. cit.*), the presence of acetic acid in the product being avoided by diminishing the quantity of acid used so as to leave the solution to be extracted with ether just alkaline with sodium hydrosulphide. Before determination of the densities and other physical constants, the substance was repeatedly distilled under diminished pressure in a current of pure carbon dioxide until the refractive index was no longer affected.

The pure substance has a faint odour, but it acquires a more pronounced and characteristic odour on keeping: it boils at  $55^\circ/13$  mm. and with slight decomposition at  $157\text{--}158^\circ/742$  mm. (Found:  $S = 41.3$ . Calc.,  $S = 41.04$  per cent.).

The following values of the density were found:  $d_4^{20} = 1.1317$ ,  $d_4^{25} = 1.1230$ ,  $d_4^{30} = 1.1143$ , which may be reproduced from the equation  $d_4^t = 1.1317 - 0.00087t$ .

The liquid is completely miscible with ether, benzene, or water. The mixture with an equal weight of water shows a contraction of 1 per cent. in volume, as compared with 3 per cent. in the case of ethyl alcohol and water.

The following values of the refractive index were observed:  $n_D^{20} = 1.4963$ ,  $n_D^{20} = 1.4996$ ,  $n_D^{20} = 1.5079$ ,  $n_D^{20} = 1.5151$ , from which the molecular refractivities were calculated as follow:  $[R_L]_a = 20.49$  (20.51),  $[R_L]_b = 20.61$  (20.65),  $[R_L]_c = 20.90$  (20.90), and  $[R_L]_d = 21.15$  (21.16), in good agreement with the values in brackets calculated from the constants of Eisenlohr and of Price and Twiss (T., 1912, **101**, 1259).

The viscosity of the liquid, determined by comparison with water in an Ostwald viscometer at 20°, was 0.0322 C.G.S. units.

*Molecular Weight in Solution and as Vapour.*—The following values were found by the cryoscopic method in benzene solution: 79.3 (1 per cent. concentration), 84.5, 90.5, 94.5 (5 per cent. concentration), whilst in aqueous solution a constant value was observed of 75–76 (Calc., 78.1).

Vapour density determinations by the Victor Meyer method at the boiling point of aniline failed owing to a slight decomposition of the substance. Determinations were made by the method of Bleier and Kohn in dry carbon dioxide gas under a pressure of 1.6 atm., and the molecular weight of the vapour was found to be 77.0, 78.3 (Calc.,  $M = 78.1$ ).

#### *Mercaptides Derived from Monothioethylene Glycol.*

An extended series of mercaptides has been obtained hitherto only from ethyl or methyl mercaptan. The derivatives of monothioethylene glycol with a number of metals were isolated, those of mercury, lead, bismuth, and antimony being obtained by the interaction of the oxide of the metal and the mercaptan, in the presence of alcohol where necessary, whilst those of copper, gold, silver, platinum, nickel, and cadmium were obtained by precipitation in aqueous solution, sodium acetate being added to remove free mineral acid. All the compounds (except the antimony derivative) are more or less soluble in hot water and alcohol. Several, particularly the mercury and the bismuth compounds, when treated in aqueous solution with hydrogen sulphide, give rise with great ease to colloidal sols of the metal sulphide of considerable concentration and stability.

Carius (*loc. cit.*) prepared the mercury compound and also observed precipitates with lead, silver, copper, and zinc solutions. His description of them does not agree with the results obtained in the present investigation. This was, however, to be expected, since his specimen of the mercaptan (which was not distilled) was far from pure, as is shown by his statement that it was not miscible with water. The mercury compound was probably the only simple derivative of the mercaptan which he obtained in a state of purity.



In a recent paper (*J. Amer. Chem. Soc.*, 1922, **44**, 634), Rosen and Reid refer to a mercurous compound of m. p.  $108^{\circ}$ , but no analysis is quoted of what would be a novel type of mercaptide. The only mercury compounds to be described here are the normal mercaptide of the formula  $\text{Hg}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$  and the mercurichloride,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{HgCl}$ .

*Mercury compound*,  $\text{Hg}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , large silvery plates, m. p.  $123^{\circ}$ , from alcohol or warm water. Soluble in warm acetone or ethyl acetate (Found:  $\text{Hg} = 56.9$ . Calc.,  $\text{Hg} = 56.7$  per cent.). The aqueous solution gave no precipitate with solutions of sodium hydroxide or potassium iodide. With hydrogen sulphide, a colloidal sol of the sulphide was formed, which was at once coagulated on addition of ammonium nitrate solution.

*Mercurichloride*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{HgCl}$ , a white solid melting indefinitely at  $135\text{--}140^{\circ}$ , obtained by precipitation of an alcoholic mercuric chloride solution with the mercaptan (Found:  $\text{Hg} = 63.4$ .  $\text{C}_2\text{H}_5\text{OClSHg}$  requires  $\text{Hg} = 64.1$  per cent.).

*Lead compound*,  $\text{Pb}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , orange plates, m. p.  $110^{\circ}$ , from alcohol, closely resembling lead iodide in appearance (Found:  $\text{Pb} = 56.0$ .  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Pb}$  requires  $\text{Pb} = 57.4$  per cent.).

*Cuprous compound*,  $\text{CuS}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , a white solid which became discoloured on exposure to light. This substance, and others mentioned below where no melting point is recorded, decomposed, when heated, without melting (Found:  $\text{Cu} = 43.9, 43.8$ .  $\text{C}_2\text{H}_5\text{OSCu}$  requires  $\text{Cu} = 45.15$  per cent.). When a cold solution of a cupric salt was treated with the equivalent weight of the mercaptan, a yellow precipitate was formed of the *cupric* compound, but this was not isolated pure. On heating with an excess of the mercaptan, it was converted into the cuprous compound described above.

*Silver compound*,  $\text{AgS}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , white solid sparingly soluble in cold water (Found:  $\text{Ag} = 57.6, 57.2$ .  $\text{C}_2\text{H}_5\text{OSAg}$  requires  $\text{Ag} = 58.3$  per cent.).

*Aurous compound*,  $\text{AuS}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , a pale yellowish-grey solid soluble in hot water (Found:  $\text{Au} = 71.5$ .  $\text{C}_2\text{H}_5\text{OSAu}$  requires  $\text{Au} = 71.9$  per cent.). When the mercaptan was added to an excess of a cold solution of auric chloride, a chocolate-brown precipitate was formed which could not be isolated pure, but was doubtless an *auric* compound (compare Heumann, *Ber.*, 1905, **38**, 2813). When the solution was heated with an excess of the mercaptan, the aurous compound was obtained.

*Platinous compound*,  $\text{Pt}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , a pale greenish-grey solid sparingly soluble in hot water (Found:  $\text{Pt} = 55.6$ .  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Pt}$  requires  $\text{Pt} = 55.87$  per cent.). With an excess of cold platinic

chloride solution, the mercaptan gave a yellow precipitate containing a platinum compound.

*Cadmium compound*,  $\text{Cd}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , a white, crystalline solid melting with decomposition at  $139^\circ$ , soluble in warm water (Found :  $\text{Cd} = 41.9$ .  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Cd}$  requires  $\text{Cd} = 42.3$  per cent.).

*Nickel compound*,  $\text{Ni}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , dark brown needles from hot water (Found :  $\text{Ni} = 27.3$ .  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Ni}$  requires  $\text{Ni} = 27.6$  per cent.). The mercaptan gave with a solution of zinc acetate a white precipitate and with cobalt acetate a purplish-brown, amorphous precipitate, the surface of the solution becoming covered with a skin having a greenish-gold, metallic appearance, but no definite compound of zinc or cobalt was isolated in a pure condition.

*Bismuth compound*,  $\text{Bi}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_3$ , lemon-yellow needles, m. p.  $79^\circ$ , from alcohol or ethyl acetate, soluble in cold water, sparingly soluble in boiling ether or benzene (Found :  $\text{Bi} = 49.1$ ,  $49.8$ .  $\text{C}_6\text{H}_{15}\text{O}_3\text{S}_3\text{Bi}$  requires  $\text{Bi} = 47.4$  per cent.).

*Antimony compound*,  $\text{Sb}(\text{OH})(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , colourless crystals, m. p.  $131^\circ$ , obtained by warming the mercaptan with antimonious oxide, diluting the solution with alcohol, and allowing to crystallise. The compound is very sparingly soluble in all solvents except the warm monothioethylene glycol itself (Found :  $\text{Sb} = 41.7$ ;  $M$ , by Rast's method in molten camphor,  $\approx 340$ .  $\text{C}_4\text{H}_{11}\text{O}_3\text{S}_2\text{Sb}$  requires  $\text{Sb} = 41.2$  per cent.;  $M = 291$ ).

*Calcium compound*,  $\text{Ca}(\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH})_2$ , a white solid obtained by adding dry ether to the mercaptan in which calcium metal has been dissolved at  $100^\circ$  (Found :  $\text{Ca} = 20.9$ .  $\text{C}_4\text{H}_{10}\text{O}_2\text{S}_2\text{Ca}$  requires  $\text{Ca} = 20.6$  per cent.).

*Monosodium compound*,  $\text{NaS}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , white, crystalline, deliquescent solid obtained by the action of metallic sodium on the mercaptan in dry ether or toluene (Found :  $\text{Na} = 23.2$ .  $\text{C}_2\text{H}_5\text{OSNa}$  requires  $\text{Na} = 23.0$  per cent.).

*Disodium compound*,  $\text{NaS}\cdot\text{C}_2\text{H}_4\cdot\text{ONa}$ , a cream-coloured, homogeneous, crystalline powder was obtained by evaporating to dryness an absolute alcoholic solution containing the calculated weights of the mercaptan and sodium metal, and finally heating the solid to  $150^\circ$  under reduced pressure to remove alcohol (compare preparation of disodium compound of glycol, Vorländer, *Annalen*, 1894, 280, 181). The substance is very deliquescent and very readily soluble in alcohol or water (Found :  $\text{Na} = 37.2$ .  $\text{C}_2\text{H}_4\text{OSNa}_2$  requires  $\text{Na} = 37.7$  per cent.).

*Potassium compound*,  $\text{KS}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , a deliquescent, white solid from metallic potassium and the mercaptan in dry ether (Found :  $\text{K} = 33.3$ .  $\text{C}_2\text{H}_5\text{OSK}$  requires  $\text{K} = 33.6$  per cent.).

*Action of Acids on Monothioethylene Glycol.*

It had already been observed that monothioethylene glycol, left with dilute hydrochloric acid, was converted into a polymeric ethylene sulphide (Bennett, *loc. cit.*). This action was slow at room temperature and with dilute mineral acids, but when the mercaptan, mixed with an excess (five times its volume) of 50 per cent. aqueous sulphuric acid, was heated to the boiling point, the solution rapidly became turbid by the separation of clear oily drops, which at once became opaque, and a bulky, white precipitate filled the liquid. A trace of a volatile substance having a penetrating smell was also produced, which may be the unpolymerised ethylene sulphide recently isolated by Delépine (*Compt. rend.*, 1920, **171**, 36). The filtrate from the white solid (*A*) thus obtained gave, on further heating, a white precipitate (*B*) which showed slightly different properties from those of *A*. Similar results were obtained when phosphoric acid was used in place of sulphuric acid. These substances, *A* and *B*, are insoluble in all the usual solvents and are similar in properties to the amorphous polymeric ethylene sulphides described by Löwig and Weidmann and by Mansfeld (*loc. cit.*), but difficulties of characterisation leave it uncertain whether identical substances (or mixtures) are in question. They were found to be soluble in molten camphor, and therefore cryoscopic measurements were made by Rast's method (*Ber.*, 1922, **55**, [B], 1051):—

*A*. White solid, melting rather indefinitely at 193—197° (Found: *S* = 53.0; *M*, in camphor, = 1430, 1760, 1420).

*B*. White solid, melting indefinitely at 177—180° (Found: *S* = 52.8; *M* = 1720.  $C_2H_4S$  requires *S* = 53.3 per cent.; *M* = 60).

*A* and *B* were distinguished chiefly by their different behaviour on heating. *A* decomposed on dry distillation to give a yellow oil of unpleasant odour, whilst *B* gave a considerable sublimate of the well-known crystalline diethylene disulphide of m. p. 112° and b. p. 200° (Found: *S* = 53.5. Calc., *S* = 53.3 per cent.). Neither *A* nor *B* yielded this substance when heated in phenol by the method described by Mansfeld (*loc. cit.*) and by V. Meyer (*Ber.*, 1886, **19**, 3262). The molecular weight determinations are a rough indication of a high degree of polymerisation. The assumption made by Mansfeld, that since his polymeride must be of higher molecular weight than diethylene disulphide its formula was  $(C_2H_4S)_3$ , is clearly unjustifiable.\*

\* A substance volatile in steam and having m. p. 113° and composition corresponding to  $(C_2H_4S)_3$  was described as triethylene trisulphide by Sir P. C. Rây (T., 1920, **117**, 1090; this vol., p. 1279). No evidence was given as to its molecular weight, and it seems very probable that the substance is diethylene disulphide, which would in any case be a probable by-product of the reaction investigated.

*Action of Dehydrating Agents.*

Monothioethylene glycol reacted vigorously with anhydrous zinc chloride or phosphoric oxide with production of amorphous, white solids similar to those described above. In the latter case a small amount of diethylene disulphide appeared as a sublimate.

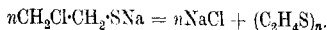
*Action of Concentrated Hydrochloric Acid.*

A mixture of monothioethylene glycol with three times its volume of concentrated hydrochloric acid was heated to the boiling point for five minutes under an upright condenser. The solution became turbid at once and a colourless oil separated. This oil was quickly washed once with water and dried over sodium sulphate.

$\beta$ -Chloroethyl mercaptan,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{SH}$ , was thus obtained (in 90 per cent. yield) as a colourless liquid, b. p.  $125\text{--}126^\circ$  (Found :  $\text{Cl} = 36.4$ ;  $\text{S} = 33.1$ .  $\text{C}_2\text{H}_5\text{ClS}$  requires  $\text{Cl} = 36.8$ ;  $\text{S} = 33.2$  per cent.). The substance may be distilled at the ordinary pressure without decomposition provided it is free from moisture. The following physical constants were observed :  $d_4^{20} = 1.225$ , and  $d_4^{25} = 1.203$ ;  $n_D^{20} = 1.5289$ , whence  $[R_L]_D = 24.74$  (Calc., 24.0).

The liquid has a marked vesicant action, which in conjunction with its volatility makes it very unpleasant to work with. When kept in a damp atmosphere, it develops a pungent odour.

$\beta$ -Chloroethyl mercaptan dissolves in an excess of aqueous sodium hydroxide to a clear solution, which, however, becomes turbid in a few seconds and rapidly sets to a paste owing to the separation of a white solid polymeric ethylene sulphide :



The white solid, after being washed with water and alcohol and dried at  $120^\circ$ , melted indefinitely at  $170\text{--}175^\circ$  (Found :  $\text{S} = 52.6$ . Calc.,  $\text{S} = 53.3$  per cent.).

The chloromercaptan, when kept in contact with cold water, or by prolonged washing, is decomposed in the same manner with production of free hydrochloric acid and a white, amorphous substance similar to that described above.

The action of concentrated hydrobromic acid upon monothioethylene glycol was similar to that of hydrochloric acid, but the oil that separated became at once turbid from the precipitation of a white solid, and the bromo-mercaptan was not isolated.

*Action of Phenylcarbimide on Monothioethylene Glycol.*

The formation of  $\beta$ -hydroxyethyl phenylthiocarbamate,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , was described in a previous paper

(Bennett and Whincop, T., 1921, **119**, 1861). When this substance or monothioethylene glycol itself was heated for a few minutes with an excess of phenylcarbimide there was produced the compound  $C_6H_5 \cdot NH \cdot CO \cdot S \cdot C_2H_4 \cdot O \cdot CO \cdot NH \cdot C_6H_5$ , which crystallised from alcohol in needles, m. p.  $146^\circ$  (Found : N = 9.1; S = 10.2.  $C_{16}H_{18}O_3N_2S$  requires N = 8.86; S = 10.14 per cent.).

*Ethylene Bis-β-hydroxyethyl Sulphide.*

This substance was described in a previous communication (Bennett and Whincop, *loc. cit.*). In view of the statement by Rosen and Reid (*loc. cit.*, footnote) that, following the directions there given, they obtained only 20 per cent. of the theoretical yield, the experiment was repeated. The temperature of the reaction mixture was kept below  $40^\circ$  until the action subsided, and was then raised to the boiling point for fifteen minutes. The alcohol was removed by evaporation, and the sodium bromide from the residue by dissolving the latter in an excess of dry ethyl acetate, filtering, and again evaporating. The crude product, dried at  $120^\circ$ , weighed 5.9 grams (yield calculated from the sodium used, 6.0 grams) and melted at  $50-55^\circ$ . After crystallisation from a little ethyl acetate, 5.5 grams of the substance were obtained, m. p.  $62-63^\circ$ . The yield is thus practically quantitative, as originally stated.

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CCLVIII.—*The Constitution of Acetone Derivatives of Glucose and Fructose.*

By JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON.

It will be generally recognised that the difficult structural problems presented by the carbohydrates can be approached only by the systematic study of specific and definite reactions. The method may be slow but, on the other hand, isolated observations followed by hasty conclusions lead inevitably to confusion. Particularly is this the case in dealing with the compounds formed when sugars, or the related polyhydric alcohols, enter into condensation with acetone. When critically examined, these derivatives display many puzzling aspects of isomerism and, in addition, their study is ham-

pered by their extreme instability towards mere traces of acids. As a result, limitations are placed on the reactions which can be applied with the object of elucidating their structure.

These "acetone-sugars" are, however, compounds of great importance, as they open the way to the preparation of definite derivatives of sugars in which certain hydroxyl groups are substituted while others remain exposed and can take part in further reactions. This application of acetone-sugars was originally developed by one of us, and examples are now given of typical cases in which, by methylation and subsequent hydrolysis, these compounds were converted into a series of partly methylated sugars, which were the first representatives of their type.

Rhamnoseacetone → Dimethyl rhamnose :

Purdie and Irvine, *Rep. Brit. Assoc.*, 1902.

Purdie and Young, *T.*, 1906, **89**, 1194.

Glucosediacetone → Monomethyl glucose :

Irvine and Scott, *T.*, 1913, **103**, 564.

Irvine and Hogg, *T.*, 1914, **105**, 1386.

Glucosemonoacetone → Trimethyl glucose :

Irvine and Scott, *loc. cit.*

Irvine and Macdonald, *T.*, 1915, **107**, 1701.

Fructosediacetone → Monomethyl fructose :

Irvine and Hynd, *T.*, 1909, **95**, 1220.

Mannitoldiacetone → Dimethyl mannitol :

Irvine and Paterson, *T.*, 1914, **105**, 898.

Mannitolmonoacetone → Tetramethyl mannitol :

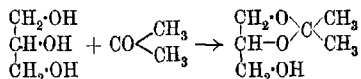
Irvine and Paterson, *loc. cit.*

Glycerolacetone → Monomethyl glycerol :

Irvine, Macdonald, and Soutar, *T.*, 1915, **107**, 337.

Fischer, who was responsible for the discovery of the general reaction between carbohydrates and acetone, returned to the subject in 1915, and, by the application of similar principles, prepared a number of partly acylated derivatives analogous to the above methylated compounds. The importance of these reactions and their ultimate applications need not be emphasised and it is evident that the constitution of all the synthetical compounds concerned rests primarily (although not invariably) on the structure of the acetone derivatives from which they are prepared. Numerous researches have therefore been devoted to this problem, and as the whole subject has been further complicated by the discovery of "γ-sugars," it is necessary at this stage to review the progress which has been made.

The collective evidence contained in the papers issued from this laboratory has established that in condensing with a polyhydroxy-compound acetone reacts as a ketone and not in the enolic form. A further definite advance was made when Irvine, Macdonald, and Soutar (*loc. cit.*) showed that the condensation involves preferentially two neighbouring hydroxyl groups. The test case selected was the formation of glycerolacetone, which was proved to take place according to the following scheme :



The above result was obtained by ascertaining that glycerolacetone can be converted into glycerol  $\alpha$ -methyl ether, and in a similar manner the methylation process has given direct evidence on the structure of the more important of the sugar acetones.

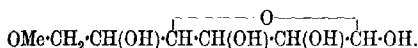
The present paper deals with the constitution of the acetone derivatives of fructose, and in addition the structure of the isomeric derivatives of glucose is reviewed in the light of the most recent observations on  $\gamma$ -sugars. Fructose gives two crystalline diacetone compounds (termed  $\alpha$ - and  $\beta$ -), and these are convertible into isomeric fructosemonoacetones (Irvine and Garrett, T., 1910, 97, 1277). In addition, other non-crystalline fructosemonoacetones exist but, in the meantime, discussion is restricted to the  $\alpha$ -forms, which are the most definite and are produced in greatest amount. On first consideration it might appear that both fructose- $\alpha$ -diacetone and fructose- $\alpha$ -monoacetone are derived from  $\gamma$ -fructose, as the rate of hydrolysis of these compounds is of the same order as that of sucrose. We have now established, however, that such is not the case and that both compounds are based on the stable type of fructose. This result was not unexpected, as both fructose-diacetone and fructosemonoacetone are laevorotatory, whereas if the compounds were related to  $\gamma$ -fructose the rotations would be dextro.

A structural formula for fructosediacetone must obviously accommodate the following conditions :

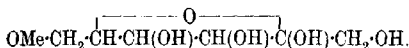
- (1) Hydrolysis to give a non-reducing fructosemonoacetone (Irvine and Garrett, *loc. cit.*).
- (2) The conversion into a laevorotatory monomethyl fructose (Irvine and Hynd, *loc. cit.*).
- (3) The identity of the phenylosazone given by the above sugar with the monomethyl glucosazone (Irvine and Scott, *loc. cit.*) obtained from glucosediacetone.

The key to the constitution therefore lies in the structure of monomethyl glucose, as the position of the methyl group in this

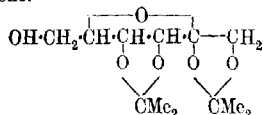
sugar corresponds with the vacant hydroxyl group in fructosediacetone. Now, it has been shown by Irvine and Hogg (*loc. cit.*) that in monomethyl glucose the alkyl group is terminal and consequently the sugar has the structure



This determines the position of the methyl group in the monomethyl fructose obtained from fructosediacetone, and as it has now been established that the fructose acetones are related to the stable type of fructose, the formula of monomethyl fructose may be written



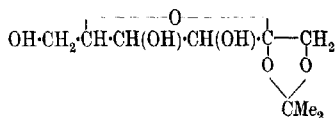
It follows therefore that if the isopropylidene residues are united through neighbouring hydroxyl groups, only one formula is possible for fructosediacetone.



Such a compound should exist in two stereoisomeric forms which should undergo hydrolysis at different rates to give two isomeric fructosemonoacetones. Irvine and Garrett (*loc. cit.*) have already shown this to be the case. There is, however, one possibility of error in the argument and the point is somewhat elusive. Fructosediacetone *might* be a derivative of  $\gamma$ -fructose, in which case the hydrolysis of monomethyl fructosediacetone would give monomethyl  $\gamma$ -fructose. Such a sugar would contain three hydroxyl groups, and the oxygen linkage has thus the opportunity to assume the stable arrangement. Analogous cases are presented by inulin and sucrose, where the evidence of hydrolysis is misleading. This possibility has not been overlooked and the extension of our work has therefore included the examination of fructose- $\alpha$ -monoacetone. When it is remembered that complete hydrolysis of fructose- $\alpha$ -diacetone takes place practically instantaneously by the action of 0.1 per cent. hydrochloric acid at 100°, the dissection of the reaction into stages is stamped as a delicate operation. The methylation of the fructose- $\alpha$ -monoacetone thus obtained also proved to be difficult, but we succeeded in converting the compound into a trimethyl fructosemonoacetone in which the levorotation was preserved. On hydrolysis, a trimethyl fructose was produced ( $[\alpha]_D$  in water - 115.9°) and this in turn was converted, as

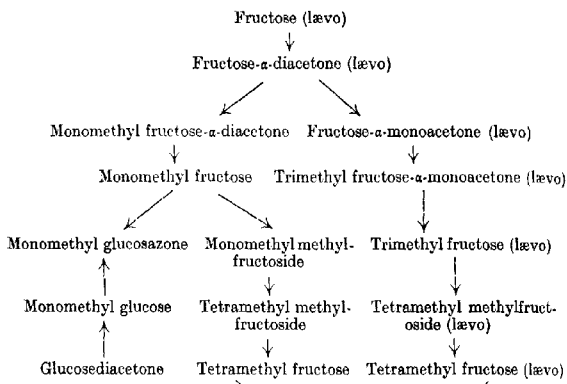


described in the experimental part, into tetramethyl fructose. The important issue of these operations is that the tetramethyl fructose finally produced is the stable, crystalline variety possessing the butylene-oxide linkage. These results establish the structure of fructosemonoacetone to be



and the compound has no relationship with  $\gamma$ -fructose.

In order to render the scheme of reactions intelligible, the various transformations involved in the structural proof are given below:



All the above fructose derivatives were lævorotatory; the two specimens of tetramethyl fructose were identical with each other and with the methylated ketose prepared by Steele (T., 1918, 113, 257) from  $\beta$ -methylfructoside. No trace of the dextrorotatory tetramethyl  $\gamma$ -fructose produced from methylated inulin or sucrose was present and the proof is clear that both fructosediacetone and fructosemonoacetone are constituted as shown.

As supplementary evidence and for the purposes of comparison, we have prepared a trimethyl fructosemonoacetone of the  $\gamma$ -series and find, as expected, that it is entirely distinct from the form referred to in the above scheme. A full account of this isomeride will be given in a subsequent paper, but it may be mentioned that the compound is dextrorotatory and gives a dextrorotatory trimethyl fructose.

There seems, in fact, to be little tendency for  $\gamma$ -fructose to con-

dense with acetone and this was emphasised by the behaviour of dextrorotatory  $\gamma$ -methylfructoside when subjected to the action of acidified acetone. The methyl group was eliminated and fructose-diacetone formed, but the product consisted entirely of the crystalline, levorotatory  $\alpha$ -form, thus showing that complete rearrangement of the oxygen linkage had taken place during the reaction. The formulæ now supported for the fructoseacetones are identical with those suggested in former papers from this laboratory, and the only structural evidence still required to complete the proof is confirmation of the idea that the stable form of tetramethylfructose possesses the butylene-oxide linkage. This evidence has been obtained and will form the subject of a forthcoming paper.

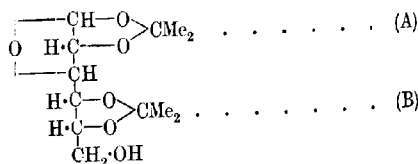
Turning to the case of the acetone derivatives of glucose, the complications encountered are more serious. The glucosediacetone isolated by Fischer melts at  $107-108^\circ$  and shows  $[\alpha]_D -18.5^\circ$ , although there is at least one other form of the compound which is also levorotatory but possesses a higher melting-point. It is in fact difficult to specify the total number of isomeric glucose-diacetones, as the compounds show a tendency to separate in mixed crystals and to combine with monoacetone derivatives. In the present discussion attention is therefore restricted to the most important variety, which may be termed the  $\alpha$ -form. Two apparently diagnostic reactions are available in deducing the structure of the compound. Of these, the first is the conversion into 6-monomethyl glucose, a change which shows that the unsubstituted hydroxyl group in the parent compound is terminal. The second, and more important, is the dissection into two stages of the hydrolysis of glucose- $\alpha$ -diacetone, a process which results in the formation of glucose- $\alpha$ -monoacetone.

As a first step in ascribing structural formulæ to the glucose-acetones, it is necessary to determine the particular isomeric form of the hexose from which the compounds are derived. In this connexion it is significant that all the acetone derivatives of glucose are strongly levorotatory, whereas in the case of the isomeric fructose compounds the sign of the rotation of the parent hexose is preserved. The activities of the compounds can be regarded at the most as an indication that the glucoseacetones are based on  $\gamma$ -glucose, but definite evidence is now available that this view is correct. The argument, although somewhat involved, is decisive. It has long been known that glucosediacetone gives a levorotatory monomethyl glucosediacetone which on hydrolysis yields a dextrorotatory monomethyl glucose belonging to the butylene-oxide series. On first inspection, this result might be interpreted as a proof that glucosediacetone is derived from the butylene-oxide type of

glucose, but, as the monomethyl glucose contains an unsubstituted hydroxyl group in the 4-position, the possibility is always open that, subsequent to liberation of the sugar, the oxygen linkage alters from the unstable to the stable position. The evidence of hydrolysis may thus be entirely misleading, as in the case of sucrose and of inulin. The only conclusive method of determining the type of the parent hexose is to convert glucosediacetone into glucosemonoacetone, to methylate this and, by hydrolysis, obtain the corresponding trimethyl glucose. If the latter belongs to the butylene-oxide type, it will be dextrorotatory and convertible into crystalline tetramethyl glucose. Otherwise, it will be levorotatory and possess the properties of a  $\gamma$ -sugar.

The operations involved are difficult, as the glucosemonoacetone must be of a high degree of purity, but trimethyl glucosemonoacetone was obtained in good yield. Hydrolysis gave a trimethyl glucose which is *levorotatory* ( $[\alpha]_D -15.7^\circ$  in water) and displays all the characteristic reactions of a  $\gamma$ -sugar. It follows that glucosemonoacetone and glucosediacetone both belong to the  $\gamma$ -series.

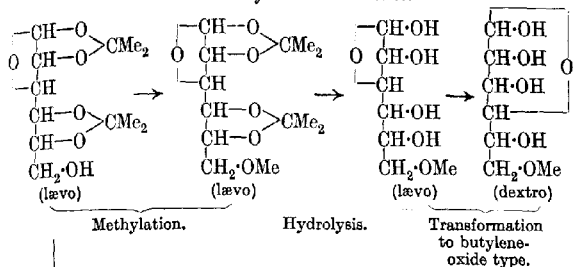
No formula hitherto suggested for the glucoseacetones takes into consideration this relationship with  $\gamma$ -glucose, and the structures must accordingly be reviewed. Unfortunately, the difficult problem of the constitution of  $\gamma$ -glucose has not yet been fully solved. Most of the evidence is in favour of an ethylene-oxide structure but, on the other hand, some reactions point more strongly to a propylene-oxide linkage. Of these two alternatives, it is clear that the propylene-oxide type is best adapted to accommodate the formation and properties of the glucose acetones. We therefore suggest the following tentative structure for glucosediacetone, from which, by removal of the isopropylidene residue B, the formula for glucosemonoacetone is derived. Although the exact position of the oxygen linkage is uncertain, and may connect positions 1 and 2 in place of 1 and 3, the structures now given are consistent with all the known reactions of these compounds.



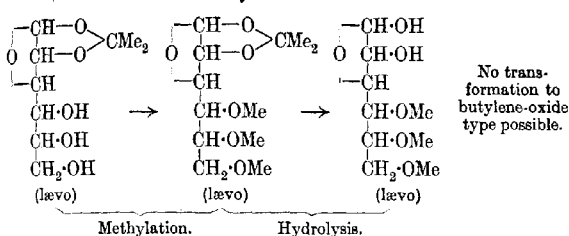
For example, the formulæ fulfil the condition that acetone condenses with neighbouring hydroxyl groups, and explain why a methylated sugar of the stable type is obtained from glucosediacetone whilst

glucosemonoacetone gives a  $\gamma$ -sugar. Incidentally also, accepting Hudson's generalisations as to the factors which control dextro- and laevo-rotation in aldose derivatives, the laevorotation of the glucoseacetones receives a ready explanation.

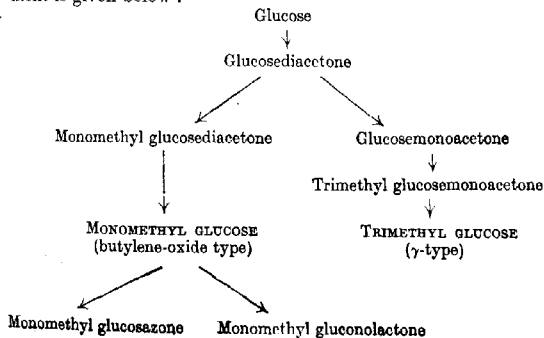
*Reactions of Glucosediacetone.*



*Reactions of Glucosemonoacetone.*



For the sake of comparison with the parallel work on fructose compounds, the scheme of reactions utilised in the structural argument is given below :



*Discussion of Results, and Criticism of Alternative Formulae.*

The most striking feature of the results submitted is that whereas fructose shows a pronounced tendency to react as a  $\gamma$ -sugar and is present in this form in its most important natural derivatives (sucrose and inulin), the fructoseacetones are derived from the butylene-oxide form of the ketose. On the other hand, although glucose is transformed less readily into its  $\gamma$ -isomeride, it is entirely in this condition that it enters into condensation with acetone. Analogy, without experiment, would have led to an entirely opposite conclusion being drawn, until it is remembered that there is an essential difference in the experimental procedure involved in preparing these compounds.

Another point which has been experimentally developed is that the oxygen linkage of a reducing sugar may alter in position to accommodate the action of a particular reagent. Thus the configuration of stable glucose is unfavourable to the formation of a diacetone derivative and accordingly transformation to the  $\gamma$ -sugar precedes condensation. No such alteration is necessary in the case of stable fructose and the condensation ensues without change in the oxygen linkage. In fact, a fructose derivative of the  $\gamma$ -type has been shown to revert to the stable linkage in the presence of acid acetone, and this case adds another example to the list of reactions which involve transformation of the oxygen linkages in sugars. Exclusive of the formation of " $\gamma$ -glucosides" the more important changes of this nature so far detected are :

Sucrose  $\rightarrow$  Fructose

Inulin  $\rightarrow$  Fructose

Monomethyl glucosediacetone  $\rightarrow$  Monomethyl glucose

$\gamma$ -Methyl fructoside  $\rightarrow$  Fructosediacetone

Glucose  $\rightarrow$  Glucosediacetone

Monomethyl methylglucoside  $\rightarrow$  Glucosediacetone.

With two exceptions, all the above changes are in the direction  $\gamma$ -type  $\rightarrow$  stable type. The most irregular case is presented by glucose, but a review of past work provides a ready explanation. It may be recalled that Macdonald, in an able study of the mechanism of the condensation of glucose with acetone (T., 1913, 103, 1896), showed that the reaction involves the formation of a methylglucoside monoacetone. At that time no  $\gamma$ -sugars had been described and thus Macdonald's formulæ cannot now be upheld, but it is clear that he succeeded in condensing  $\gamma$ -methylglucoside with acetone. This is shown by the fact that the methylglucoside monoacetone is laevorotatory, gives a laevo-dimethyl derivative, and is hydrolysed with extreme ease under conditions which affect

$\gamma$ -glucosides. It is significant that an isomeric methylfructoside monoacetone exists (Irvine and Robertson, T., 1916, 109, 1305) which is strongly laevorotatory, and the formation of these compounds gives a clue to the mechanism whereby the corresponding diacetones are formed.

Those who have the widest experience of the compounds now under discussion are probably the most reluctant to commit themselves to opinions as to their structure. Although no finality is claimed for the formulæ now deduced for the glucose and fructose acetones, it is nevertheless necessary to criticise severely certain structures confidently put forward in a recent paper by Karrer and Hurwitz (*Helv. Chim. Acta*, 1921, 4, 728). Unless their conclusions are corrected in no uncertain fashion, this branch of structural chemistry may again be thrown into a state of hopeless confusion.

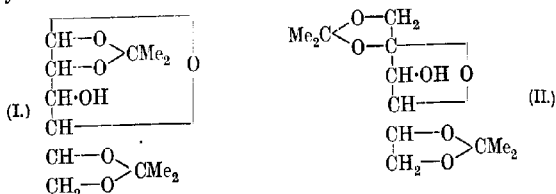
The authors referred to have compared the effect of alkaline potassium permanganate on three well-known acetone sugars with the action of the same reagent on glycerolacetone, which is known to have the terminal  $\text{CH}_2\text{-OH}$  group free. The argument used is that if the sugar derivative does not reduce the reagent readily the terminal hydroxyl group must be substituted. On the basis of four small-scale experiments in which glucosediacetone, fructose-diacetone, and  $\beta$ -mannitoldiacetone are boiled with the permanganate reagent and recovered largely unchanged, they proceed to reconstruct the constitution of acetone sugars generally. The structures they put forward for the glucose- and fructose-acetones are not only shown to be incorrect by the results contributed in this paper, but are opposed to many reactions which have long been known. So many objections may be taken to their views that it is needless to refer to them in detail, but the following points may be mentioned.

Alkaline potassium permanganate is a particularly uncertain reagent when applied to derivatives of sugars. To illustrate the vagaries of the reaction, two examples may be quoted. 1:2:3:4-Tetramethyl-5-ethyl mannitol has a terminal hydroxyl group free, yet is remarkably stable towards the action of potassium permanganate in the presence of sodium hydroxide. On the other hand, a recrystallised specimen of tribenzylidene mannitol, which contains no unsubstituted hydroxyl group, reduces the reagent readily.

Not only is Karrer's reagent inapplicable, but his choice of glycerol-acetone as a test substance is unfortunate. Few compounds can compete with the derivatives of the trihydroxypropane series in respect of their power to reduce alkaline potassium permanganate,

and in the case of glycerolacetone the reducing action is much increased by the presence of impurities which are not readily removed by distillation. Further, an account is given in the experimental part of the preparation of a specially pure specimen of glycerolmonoacetone, which was converted into the corresponding monomethyl ether. Although in this compound all the hydroxyl groups are substituted, it decolorises alkaline permanganate readily. The bearing of these results on Karrer's generalisation need not be elaborated.

Little need be said regarding the structures which are arrived at by such methods. Glucosediacetone is formulated by Karrer as (I).



This is incorrect in two particulars and represents the compound as a derivative of butylene-oxide glucose, which is certainly not the case. Further, on methylation and hydrolysis, it would give 3-monomethyl glucose in place of 6-monomethyl glucosc. Incidentally, Karrer is evidently unacquainted with the paper by Irvine and Hogg on the structure of this variety of monomethyl glucose and is apparently of the opinion that it can be obtained from fructose-diacetone.

Similar arguments exclude Karrer's formula for glucosemonoacetone, as methylation would then give 3:5:6-trimethyl glucose. It is in some ways regrettable that this is not the case, as many unsuccessful attempts have been made to obtain this particular sugar, which is so far quite unknown.

The case for the structure of the fructose acetones may be briefly dismissed. Karrer's formula for fructosediacetone (II) is based on a propylene-oxide ketose. The suggestion of a 2:4-oxygen ring agrees with Böseken's view as to the nature of the internal oxygen linkage in the fructose component of sucrose (*Rec. trav. chim.*, 1921, 40, 354). In other words, Karrer's fructosediacetone is a derivative of  $\gamma$ -fructose. If so, it would be dextrorotatory and would give a dextro-fructosemonoacetone. This, in turn, would be convertible into trimethyl  $\gamma$ -fructosemonoacetone, which would also be dextro. No single one of these conditions is fulfilled. The trimethyl fructose actually obtained is lævo, and is convertible into crystalline tetramethyl fructose.

The paper now under discussion leads up to the statement that "the new formulæ for glucosediacetone and fructosediacetone render necessary a new nomenclature for the derivatives prepared from them." It would be unfortunate if the numerical method of indexing the position of substituents in the sugar chain, which was first proposed by one of us several years ago (Irvine, P., 1913, 29, 69), were in any way dependent on the accuracy of the formulæ which have rendered its adoption a necessity.

All the examples quoted by Karrer in illustrating the use of the numerical method are incorrect, as the substituents are placed in the wrong position. Eight out of the ten formulæ show substituting groups in the 3-position. In each case this has been arrived at through the mistaken idea that in monomethyl glucose the alkyloxy-group is attached to the third carbon atom of the chain. There is no evidence, beyond Karrer's statement that it is so, in favour of such a structure, and experimental results clearly indicate the 6-position. The remaining two examples he gives refer compounds to  $\gamma$ -fructose, a unit which is not present.

#### EXPERIMENTAL.

##### *Conversion of $\alpha$ -Fructosediacetone into Fructosemonoacetone.*

The fructosediacetone required was prepared essentially as described by Irvine and Hynd (*loc. cit.*), but in view of the marked instability of the compound towards acids it was found advisable to have a small quantity of finely powdered barium carbonate present when solutions were heated or concentrated. Even after careful neutralisation, crude acetone sugars show a tendency to develop acidity when heated in solution, and this precaution is necessary to obtain satisfactory yields, as otherwise hydrolysis takes place to a considerable extent. The product was recrystallised, first from low-boiling petroleum containing a little ether, and finally from light petroleum alone.

The partial hydrolysis of fructosediacetone was conducted under the conditions laid down by Irvine and Garrett (*loc. cit.*), a solution in 0.1 per cent. hydrochloric acid being preserved at 30°. It is noteworthy, as an example of the difficulty in obtaining uniform preparations of fructoseacetones, that the constant rotation (calculated on the weight of material taken initially) when the semi-hydrolysis was complete was  $[\alpha]_D - 123^\circ$ . This is 5° lower than that found by Irvine and Garrett, and the difference was also detectable in the fructosemonoacetone finally isolated. After two crystallisations from ether and one from ethyl acetate, the compound melted at the correct figure (120–121°), and the melting point showed no depression when the compound was mixed with an



authentic specimen. The specific rotation in aqueous solution was, however,  $[\alpha]_D^{20} = 145.0^\circ$  in place of  $-158.9^\circ$ . As fractional crystallisation yielded crops showing uniformly the same activity, it appeared that the preparation was optically homogeneous, but a result described later shows that this was not the case (Found: C = 49.15; H = 7.28.  $C_9H_{16}O_6$  requires C = 49.09; H = 7.27 per cent.).

*Trimethyl Fructosemonoacetone.*

Fructosemonoacetone (1 mol.) was dissolved in the minimum quantity of methyl alcohol to effect solution, and alkylated in the usual way with silver oxide (3 mols.) and methyl iodide (6 mols.). Initially, half the total amount of silver oxide was used and the heat of reaction was then sufficient to maintain the solvent at the boiling point for one hour. When this spontaneous reaction had subsided, the remainder of the oxide was added and the process was completed by heating on a water-bath for eight hours. The product was extracted with boiling ether and, after filtration, the solution invariably deposited a crystalline crop amounting to about 20 per cent. of the material subjected to methylation. This was removed and after recrystallisation from ether was shown to be unchanged fructosemonoacetone (Found: C = 48.92; H = 7.28. Calc., C = 49.09; H = 7.27 per cent.). The constants determined on this specimen now agreed closely with those recorded by Irvine and Garrett (m. p.  $120-121^\circ$ ,  $[\alpha]_D^{20}$ , in water,  $-156.8^\circ$ ) so that the fructosemonoacetone originally used was a mixture of stereoisomerides. When subjected to further methylation, this recovered material behaved normally and yielded the corresponding trimethyl derivative.

After isolating the syrup contained in the ethereal extract described above, it was subjected successively to a second and a third methylation in which the same proportions of alkylating reagents were employed, no extraneous solvent being, however, necessary in either case. Distillation under diminished pressure yielded a colourless syrup, but as the indefinite boiling point showed that the methylation was incomplete, three further alkylations were given before systematic fractional distillation was attempted. The pure compound was a mobile liquid (b. p.  $135-138^\circ/10$  mm.:  $n_D^{20}$  1.4575) which showed a wide range of solubility and behaved as a glucoside towards Fehling's solution [Found: C = 54.73; H = 8.33; OMe = 32.2.  $C_9H_{13}O_3(OMe)_3$  requires C = 54.98; H = 8.39; OMe = 35.5 per cent.].

$[\alpha]_D^{20}$ , in water,  $-147.9^\circ$  for  $c = 0.902$ .

$[\alpha]_D^{20}$ , in ethyl alcohol,  $-125.7^\circ$  for  $c = 0.887$ .

$[\alpha]_D^{20}$ , in acetone,  $-125.0^\circ$  for  $c = 1.208$  per cent.

*Conversion of Trimethyl Fructosemonoacetone into Tetramethyl Fructose.*

*Stage I.—Hydrolysis.* A 4 per cent. solution of trimethyl fructosemonoacetone in 0.1 per cent. aqueous hydrochloric acid was hydrolysed by heating at 80°. The reaction was complete in two and a half hours, the specific rotation having then diminished to  $-100^\circ$ , and was arrested by shaking with silver carbonate. Thereafter the filtered solution was heated with charcoal for one hour at 60°, again filtered, and the solvent evaporated under diminished pressure. Trimethyl fructose was thus obtained as a viscous syrup ( $[\alpha]_D^{20}$  in water,  $-115.9^\circ$ ).

*Stage II.—Condensation with methyl alcohol.* A solution of trimethyl fructose in methyl alcohol containing 0.22 per cent. of hydrogen chloride was heated at 40° for four hours, when the rotation became constant. The solvent employed was entirely free from acetone, as otherwise acetone derivatives of fructose were regenerated in the condensation. After neutralisation with silver carbonate, treatment with charcoal, and removal of the solvent under diminished pressure, trimethyl methylfructoside remained as a colourless syrup.

*Stage III.—Methylation.* The fructoside was twice methylated in the customary manner with silver oxide (3 mols.) and methyl iodide (6 mols.), the product being isolated at this stage and distilled. In this way, non-volatile by-products which resisted methylation were eliminated. After a third methylation, tetramethyl methylfructoside was obtained as a colourless liquid, b. p. 130—134°/11 mm.

*Stage IV.—Hydrolysis.* The subsequent hydrolysis was carried out in the usual manner by heating for one hour at 100° with 1.2 per cent. hydrochloric acid. The sugar finally isolated crystallised in the characteristic form of tetramethyl fructose and, after purification from light petroleum, gave correct analytical figures and the physical constants accepted as the standards for this sugar (m. p. 95—97°;  $[\alpha]_D^{20} = -87.3^\circ$  in water).

*Condensation of  $\gamma$ -Methylfructoside with Acetone.*

$\gamma$ -Methylfructoside ( $[\alpha]_D^{20} + 16^\circ$  in ethyl acetate), when boiled for three hours with excess of pure acetone, dissolved only to a slight extent and failed to condense with the solvent. On the other hand, reaction took place when the fructoside was shaken in the cold with twenty times its weight of acetone containing 0.2 per cent. of hydrogen chloride. After twenty hours' treatment, the liquid was neutralised with lead carbonate, filtered, and, in the

presence of barium carbonate, evaporated to dryness. The product immediately crystallised completely and, after recrystallisation, proved to be identical with Fischer's  $\alpha$ -fructosediacetone (m. p. 119–120°;  $[\alpha]_D$ , in water,  $-160.1^\circ$ ). As the  $\gamma$ -methylfructoside used was not entirely dissolved in the acid acetone, the yield was of the order 60 per cent., but it is evident that the reaction involves a complete alteration in the position of the oxygen ring.

*Conversion of Glucosediacetone into Trimethyl- $\gamma$ -glucose.*

The first stage in the series of reactions was the preparation of glucosemonoacetone by the semi-hydrolysis of glucose- $\alpha$ -diacetone. This was carried out according to the method described by Irvine and Macdonald (*loc. cit.*) and gave satisfactory results. Subsequent alkylation and conversion into trimethyl glucosemonoacetone was conducted in the manner adopted by Irvine and Scott (*loc. cit.*), whose results were confirmed. Hydrolysis was effected by means of 0.5 per cent. hydrochloric acid, the sugar being isolated in the usual manner and purified by distillation in a high vacuum (b. p. 153°/0.15 mm.) (Found: C = 48.51; H = 8.05; OMe = 42.8.  $C_9H_{18}O_6$  requires C = 48.64; H = 8.10; OMe = 41.2 per cent.). The methylated sugar was a colourless liquid which reduced neutral permanganate readily and rapidly precipitated yellow cuprous oxide from Fehling's solution in the cold. The compound was levorotatory in water and in organic solvents ( $[\alpha]_D$ , in alcohol,  $-37.3^\circ$ ). The levorotation was preserved in the corresponding glucoside, and the compound thus belongs to the  $\gamma$ -series.

*Action of Alkaline Potassium Permanganate on Glycerol Derivatives.*

This reaction was studied for reasons given in the introduction. The glycerolacetone employed was prepared by the improved method recommended by Fischer (*Ber.*, 1920, **53**, [B], 1606). After fractionation, a specimen which showed the correct physical constants was nevertheless very rapidly oxidised by potassium permanganate in the presence of alkali. The material also reduced neutral permanganate, a result which is due essentially to the presence of impurities.

This is shown by the fact that 0.25 gram of the first fraction collected decolorised 10 c.c. of the neutral reagent instantaneously, but this reaction was much diminished after four successive distillations, in which the first fractions were neglected. The material thus obtained gave the following results:

0.25 Gram, dissolved in water, decolorised 0.3 c.c. of *N*/10-neutral permanganate in five minutes: on adding a further 0.2 c.c., the colour persisted for twenty minutes.

0.25 Gram, dissolved in water containing two drops of 2*N*-sodium hydroxide, failed to decolorise 40 c.c. of *N*/10-potassium permanganate in one hour.

0.25 Gram, dissolved in water containing 15 drops of 2*N*-sodium hydroxide, decolorised 40 c.c. of *N*/10-permanganate in ten minutes.

Further purification of glycerolmonoacetone was effected by shaking the above material with excess of neutral *N*/10-permanganate solution for ten minutes. The liquid was extracted with ether, the extract dried, and the solvent removed. Eighty per cent. of the glycerolacetone used was obtained on distillation (b. p. 85°/12 mm.) as a clear liquid possessing a faintly pleasant smell and entirely devoid of the acrid odour of previous specimens. The compound was now almost completely stable towards neutral permanganate.

0.20 Gram decolorised 0.2 c.c. of *N*/10-permanganate in three minutes. On adding a further 0.15 c.c., the colour persisted for forty minutes, and a total addition of 0.8 c.c. was not reduced in fifteen hours.

Towards alkaline permanganate the reducing action was practically instantaneous.

The above specimen of glycerolmonoacetone was converted into monomethyl glycerolacetone by the silver oxide reaction, and the product purified by distillation.

0.200 Gram did not decolorise 0.5 c.c. of neutral *N*/10-permanganate in twenty minutes.

0.200 Gram decolorised 10 c.c. of faintly alkaline *N*/10-permanganate instantaneously. Thereafter the reduction proceeded so rapidly that the colour changes prevented an accurate titration being made.

The authors express their indebtedness to the Department of Scientific and Industrial Research for a grant which enabled one of them to take part in the investigations.

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### CCLIX.—*The Constitution of Soap Solutions. Hexadecanesulphonic (Cetylsulphonic) Acid and other Sulphonates.*

By MABEL HARRIET NORRIS.

HEXADECANESULPHONIC ACID,  $C_{16}H_{33}\cdot SO_3H$ , is an example of a hydrogen soap, and its study is of especial interest because the disturbing factor of hydrolysis is eliminated. Its hot aqueous

solutions froth readily and possess a definite detergent action. It will be shown that it is a typical example of a colloidal electrolyte, even more colloidal than sodium palmitate or stearate.\*

#### EXPERIMENTAL.

##### *Hexadecanesulphonic Acid.*†

This sulphonic acid and its derivatives have been prepared only by Reyehler (*Bull. Soc. chim.*, 1913, **27**, 110, 217, 300), who obtained the acid by oxidising the corresponding mercaptan, prepared from hexadecyl iodide. The formation of the mercaptan is quantitative, but the acid obtained is poor in quality and small in amount (30 to 50 per cent.). Many unsuccessful attempts were therefore made to prepare the latter by using sulphite or bisulphite with solvents such as water, methyl and ethyl alcohols, acetone, and ether, but these led only to such substances as hexadecyl alcohol and hexadecane.

Hexadecyl mercaptan was oxidised with potassium permanganate, excess of the latter removed with oxalic acid, the solution filtered, and the residue washed with hot water. A small quantity of oil (dihexadecylsulphone) was removed by filtration. The lead salt, precipitated by treating the hot, slightly alkaline, aqueous solution with lead acetate, having been washed with hot water and hot alcohol, was suspended in hot alcohol, and the acid isolated by passing hydrogen sulphide, filtering, and evaporating off the alcohol. The product resembles soft soap, and is at first white or slightly yellow, but on exposure to the air or when the attempt is made to drive off all the alcohol by heating, it turns brownish-black without, apparently, its other properties being affected. For the present purpose, it was found advisable not to drive off all the alcohol, but to ascertain the concentration of the various aqueous solutions by titration in aqueous alcohol. The concentrations found are expressed in weight normalities referred to 1000 grams of water.

0.75*N*-Hexadecanesulphonic acid is a white or pale yellow, sticky paste at room temperature and often has a shimmering appearance owing to the presence of micro-crystals. 0.1*N*—0.02*N*.—Solutions have the consistence of boiled starch solution, and more dilute solutions are limpid and milky. All the solutions froth readily on warming and shaking. On heating to 90°, a 0.75*N*. solution becomes quite mobile, although frequently small pieces of transparent or translucent jelly segregate. None of the solutions

\* For references, see this vol., pp. 621, 1101.

† The preparative work was carried out by Mr. D. J. Gould.

is quite clear at  $90^\circ$ , even a  $0.003N_w$ -solution being slightly milky. The milkiness appears to be due to a small amount of colloidal impurity which, in the most concentrated solutions, has a tendency to rise to the surface on long standing at  $90^\circ$ . For the ultra-microscopic appearance, reference should be made to "The Ultra-microscopic Structure of Soaps" (*Proc. Roy. Soc.*, 1921, [A], 98, 395).

*Dew Point and Conductivity.*

All measurements were carried out at  $90^\circ$  by the methods previously described. Great difficulty was at first experienced in obtaining results with the dew-point apparatus owing to tarnishing of the silver by traces of hydrogen sulphide given off from the solution of hexadecanesulphonic acid. This caused a lag in the appearance of the line which increased with increasing amount of tarnish because of decreasing visibility, and therefore the apparent alteration in the temperature observed with pure water amounted to between  $0.1^\circ$  and  $0.36^\circ$  below that found with a polished tube. The appearance and the disappearance of the line were, however, quite definite, and gave concordant series of readings. Hence, a measurement was made with pure water immediately after that with each soap solution, without altering the silver tube; the difference gave the dew-point lowering directly. The assumption that the reproducible results thus obtained are correct is supported by the fact that all these values lay between those previously obtained for the behenate and stearate (McBain and Salmon, *loc. cit.*, Fig. 3).

Table I contains the results together with the van't Hoff " $i$ " factor and the concentration of crystalloidal material calculated by dividing the dew-point lowering by  $0.483^\circ$ .

TABLE I.

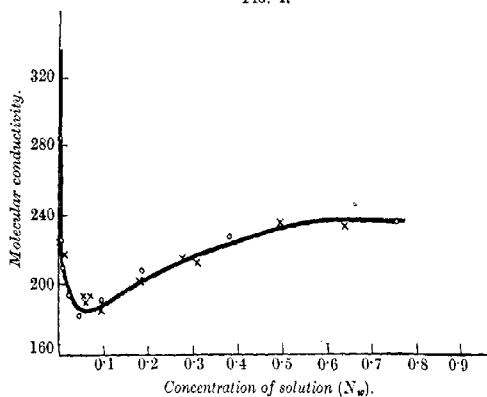
Osmotic activity of solutions of hexadecanesulphonic acid at  $90^\circ$ .

Solution ( $N_w$ ).	$\Delta^\circ$ .	$i$ .	Total crystalloid ( $N_w$ ).
0.7573	0.13	0.38	0.27
0.6412	0.14	0.45	0.29
0.500	0.125	0.52	0.26
0.3106	0.12	0.80	0.25
0.2789	0.11	0.82	0.23
0.1854	(0.08)	(0.89)	(0.17)
" by extrapolation		1.00	0.19

The results of conductivity and density measurements at  $90^\circ$  are collected in Table II and Fig. 1. A complete series of measurements was first made (indicated by circles on the diagram) and then a duplicate series in which the concentrations of the solutions fell between those used in the first series (represented by crosses),

five or six readings being taken in each case.  $\mu_{\infty}$  is taken as 702, calculated from measurements of the conductivity and the temperature coefficient of hydrochloric acid by Noyes. Reichler (*Bull. Soc. chim.*, 1913, 27, 113), who worked at 56°, could only investigate solutions from  $N/8$  downwards, but even his results show a minimum conductivity at about  $N/25$ .

FIG. 1.



Molecular conductivity of aqueous solutions of hexadecanesulphonic acid at 90°.

TABLE II.

Conductivity of solutions of hexadecanesulphonic acid at 90-90°.

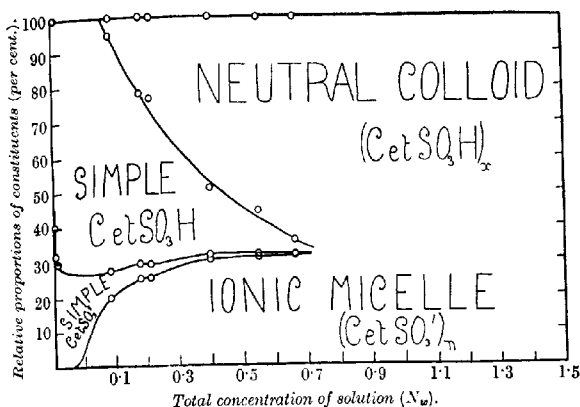
$N_w$	$d_4^{20}$	Specific conductivity.	$\mu$ .	$\alpha$ per cent.
* 0.7573	0.9596	0.1402	237.0	33.76
0.6412	0.9597	0.1217	233.7	33.30
0.4962	0.9610	0.09762	235.8	33.59
* 0.3809	0.9624	0.075004	227.4	32.40
0.3106	0.9625	0.05780	211.6	30.14
0.2789	0.9631	0.05306	214.6	30.57
* 0.1854	0.9636	0.03523	207.7	29.59
0.1824	0.9640	0.03361	201.6	28.72
0.09694	0.9646	0.016896	185.0	26.86
* 0.09618	0.9647	0.01726	190.7	27.17
0.07031	0.9650	0.01280	192.8	27.47
0.06220	0.9650	0.01118	189.5	27.01
0.05678	0.9650	0.01043	193.4	27.55
* 0.04844	0.9650	0.008397	181.9	25.91
* 0.02477	0.9652	0.004610	193.7	27.60
0.01746	0.9652	0.003651	217.2	30.94
* 0.01284	0.9653	0.002592	209.7	29.87
* 0.007298	0.9653	0.001592	225.1	32.07
0.004432	0.9653	0.0009703	223.4	31.83
* 0.003561	0.9653	0.0009791	284.3	40.81

\* = first series.

*Discussion of Results.*

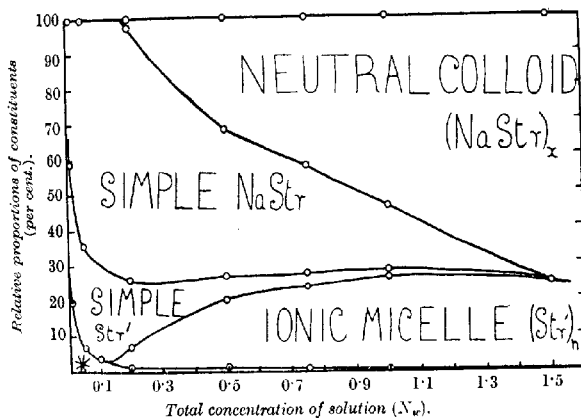
Hexadecanesulphonic acid resembles sodium palmitate and other colloidal electrolytes in possessing a high temperature coefficient

FIG. 2.



The relative proportions of the various constituents of solutions of hexadecanesulphonic acid at  $90^\circ$ .

FIG. 3.



The relative proportions of the various constituents of solutions of pure sodium stearate at  $90^\circ$ . (The asterisk \* marks the field showing the proportion of acid soap,  $2\text{NaStr} \cdot \text{HStr}$ , present.)



of solubility and in being only moderately dissociated (27 per cent. in  $0.1N_{\infty}$  solution). The anomalous form of the conductivity curve also resembles that of the soaps.

Methods described in previous communications being employed, and the dissociation constant of the simple crystalloidal soap being taken as 0.0255, the amounts of the various constituents present in these solutions have the values shown in Table III and Fig. 2. Fig. 3, which presents the data now calculated for sodium stearate by this new method ( $K = 0.06$ ), shows very clearly the resemblance between hexadecanesulphonic acid and the typical soaps; indeed hexadecanesulphonic acid is more colloidal than sodium palmitate or even stearate, coming between the latter and the behenate.

TABLE III.

The constituents of solutions of hexadecanesulphonic acid at  $90^{\circ}$ .

Solution ( $N_{\infty}$ ).	Total crystalloid.	H'.	Ionic micelle.	Simple ion.	Simple molecules.	Neutral colloid.
0.7573	0.27	0.2393	0.2381	0.0012	0.0295	0.4885
0.6412	0.29	0.203	0.198	0.005	0.082	0.356
0.4962	0.26	0.1565	0.150	0.006	0.097	0.242
0.3106	0.25	0.091	0.079	0.012	0.147	0.073
0.2789	0.23	0.082	0.070	0.012	0.136	0.061
0.1854	0.19	0.051	0.037	0.014	0.125	0.009
0.01284		0.003836	0.00	0.003836	0.0090	0.00
0.007298		0.00234	0.00	0.00234	0.004957	0.00
0.003561		0.001442	0.00	0.001442	0.002119	0.00

*Comparison with Ring Compounds Containing the  $-\text{SO}_3\text{Na}$  Group.*  
(Experimental work by Miss D. H. FALKNER and Miss M. C. PRICE.)

The following observations, made in 1919, although of a preliminary character, afford very interesting comparisons between the behaviour of the long-chain paraffin compounds and the corresponding ring compounds with the same number of atoms. They appear to open out a promising field for investigation, provided that compounds of sufficient solubility are chosen for study.

The experiments were carried out in duplicate with the usual precautions, but no special care was taken to purify the materials, which had been obtained from Kahlbaum. The following are the approximate solubilities of these substances at  $85^{\circ}$ : sodium  $\alpha$ - and  $\beta$ -naphthalenesulphonates, 32 grams; sodium naphthionate, 27 grams; and sodium anthraquinonesulphonate, 3 grams per 100 c.c. Conductivity was determined at  $25^{\circ}$  and at  $90^{\circ}$ ,  $\mu_{\infty}$  being assumed as 77.6 and 231 respectively. Only enough of the ebullioscopic data is given to illustrate the form of the curve.

TABLE IV.

Conductivity of aqueous sodium  $\alpha$ -naphthalenesulphonate at 25°.

$N_w$ .....	0.4	0.2	0.1	0.05	0.025	0.0125
$d_w^{25}$ .....	1.024	1.0115	1.004	1.000	0.999	0.998
$\mu$ .....	45.88	50.02	53.88	55.49	57.92	60.41
$a$ .....	59.13	64.46	69.42	71.50	74.64	77.84

TABLE V.

Rise in boiling point of aqueous sodium  $\alpha$ -naphthalenesulphonate.

$N_w$ .....	0.2374	0.3141	0.469	0.7208	0.936	1.663
$\Delta^b$ .....	0.195	0.245	0.360	0.540	0.670	1.120
$\frac{1}{2}$ .....	1.640	1.557	1.532	1.496	1.429	1.345

TABLE VI.

Rise of boiling point of aqueous solutions of sodium  $\beta$ -naphthalenesulphonate.

$N_w$ .....	0.2091	0.6695	0.9593	1.090	1.253	1.573
$\Delta^b$ .....	0.14	0.425	0.60	0.675	0.755	0.92
$\frac{1}{2}$ .....	1.337	1.268	1.248	1.236	1.203	1.163

TABLE VII.

Conductivity of aqueous sodium anthraquinonesulphonate at 90°.

$N_w$ .....	0.25	0.20	0.125	0.0625
$d_w^{90}$ .....	0.9815	0.9783	0.9733	0.969
$\mu$ .....	146.40	151.7	160.6	173.5
$a$ .....	63.95	66.25	70.13	75.75

Table VIII contains conductivities of these sulphonates and of sodium naphthionate at 90°, giving an approximate measure of the concentration of sodium ions present, whilst from boiling point determinations is known the total crystalloidal, the difference being the total crystalloidal material other than sodium, and the difference between this and the weight normality showing the amount of colloidal matter present. Included for comparison are the results taken from previous publications for potassium decaoctoate with the same number of carbon atoms, and also the data for potassium hexoate.

Although no stress can be laid on the accuracy of results in Table VIII, very interesting relationships are apparent. In the first place, there is very little colloid present in solutions of the salts of the ring compounds as compared with those derived from the corresponding paraffin chains. The primary consideration appears to be the length of the molecule (compare McBain, Third Colloid Report of the British Association for the Advancement of Science, 1920, p. 20). This brings out very strikingly the comparison between the otherwise almost identical naphthalenesulphonates where the longer molecules of the  $\beta$ -compounds in

TABLE VIII.

Conductivity, osmotic activity, and colloidal content of aqueous solutions of sodium  $\alpha$ - and  $\beta$ -naphthalenesulphonates and sodium naphthionate at 90°.

	$N_{90}$	$d_4^{90}$	$\mu$	$N_{\alpha}$	Crystalloid.		Total
					Total.	Less $N_{\alpha}$ .	
$\alpha$ -C <sub>10</sub> H <sub>7</sub> SO <sub>2</sub> Na ....	2.0	—	98.0	0.848	2.65	1.80	0.20
	1.0	1.0325	118.6	0.513	1.42	0.91	0.09
	0.4	—	—(25°)	0.24	0.63	(0.38)	(0.02)
	0.2	—	—(25°)	0.13	0.32	(0.19)	(0.01)
$\beta$ -C <sub>10</sub> H <sub>7</sub> SO <sub>2</sub> Na ....	1.0	1.033	124.9	0.54	1.25	0.71	0.29
C <sub>10</sub> H <sub>6</sub> (NH <sub>2</sub> )SO <sub>2</sub> Na	1.0	1.032	94.4	0.409	—	—	—
Potassium decaate	1.0	—	—	—	—	—	0.44
"    hexoate	1.0	—	—	—	—	—	0.15
"    decoate	0.2	—	—	—	—	—	0.00

*N*-solution give rise to three times as much colloid as the broader molecules of the  $\alpha$ -isomerides. This is in accordance with conclusions derived from the study of the closely related subject of liquid crystals.

The relative insolubility of sodium anthraquinonesulphonate made it impossible to obtain data for similarly concentrated solutions, but the boiling-point data gave clear indication of the presence of much more colloid in these than in the naphthalene derivatives, as would be expected from the configuration of the molecule. When much colloid is present, the Beckmann method here used is inapplicable and recourse must be had to the method of dew-point lowering.

#### Summary.

1. Hexadecanesulphonic acid is a hydrogen soap having the typical behaviour of a colloidal electrolyte in its conductivity, osmotic activity, and high temperature coefficient of solubility. Its place is amongst the highest soaps, between sodium stearate and behenate.

2. The behaviour of sodium  $\alpha$ - and  $\beta$ -naphthalenesulphonates and of sodium anthraquinonesulphonate lends support to the assumption that the length of the molecule is an important factor in producing a colloidal electrolyte. Thus the  $\alpha$ -form is less colloidal than the  $\beta$ -form, and the ring compounds are far less colloidal than the open-chain compounds with the same number of carbon atoms.

My thanks are due to Professor J. W. McBain, at whose suggestion this work was carried out, and to the Colston Research Society of the University of Bristol and the Research Fund of the Chemical Society for grants for materials.

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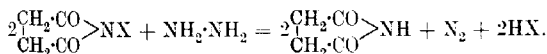
[Received, July 29th, 1922.]

CCLX.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part V. The Action of Hydrazine on the Halogen Derivatives of some Esters and Substituted cycloHexanes.*

By EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH.

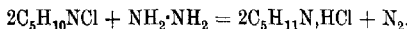
IN previous papers of this series (this vol., pp. 892, 904, 1109, 1116), it was shown that under certain conditions of molecular structure the halogen atom in organic compounds may readily be removed by the action of reducing agents. The hypotheses proposed by various workers to account for this reactivity appeared unsatisfactory, but an explanation derived from the point of view of the polarities of the constituent atoms of the molecule and the alternate effect in the carbon chain led to the conclusion that halogen atoms susceptible to reduction are endowed with an induced electro-positiveness, and their specific chemical properties are connected with this factor. In this paper, the action of hydrazine hydrate on a further series of representative substances is discussed, and additional evidence in favour of the above view is submitted.

It has already been pointed out that nitrogen-halogen compounds are very reactive, decomposing hydrazine hydrate in the cold with the quantitative liberation of nitrogen. The substances of this type previously examined were compounds such as *N*-chloroacetanilide, acetobromoamide, and sulphonechloroamides. In these, disregarding the polarity of the nitrogen atom itself, the lability of the halogen atom is due to the influence of the adjacent carbonyl or sulphonyl group. It is to be expected that if the reaction is connected with the polarity of the oxygen atoms in the carbonyl groups, the introduction of a second carbonyl group in the  $\alpha$ -position to the nitrogen atom would increase the reactivity of the halogen. This view may readily be tested, for the required conditions are realised in compounds such as succinbromimide; and these are found to be exceptionally reactive, liberating nitrogen quantitatively from hydrazine in accordance with the equation

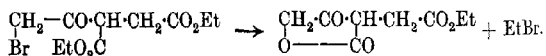


The reaction is of so vigorous a nature that it takes place with explosive violence when a few drops of a 50 per cent. solution of hydrazine hydrate are added to a little of the dry succinchloro- or succinbromo-imide; the expected increase in reactivity is thus borne out.

Although the halogen atom in nitrogen-halogen compounds is readily acted upon by reducing agents when carbonyl or sulphonyl groups are present in the  $\alpha$ -position to the nitrogen atom, it would appear that the presence of such groups is not essential to cause lability. It is true that the halogen becomes more labile on account of the influence of such groups, but the nitrogen atom itself is electronegative, and in virtue of this a halogen atom attached to it acquires an electropositiveness sufficient to make it easily removable in the presence of a suitable reagent. *N*-Tetrachloroethylenediamine, for example, is reduced by potassium iodide and acetic acid with the quantitative liberation of iodine (Chattaway, T., 1905, 87, 145), and 1-chloropiperidine is acted upon by hydrazine hydrate with the steady evolution of nitrogen in accordance with the equation

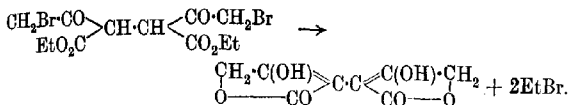


In extension of the results obtained with the series of bromo-malonic esters (this vol., p. 904), it seemed of interest to examine the bromo-derivatives of the acetylsuccinic esters. If these are brominated in the  $\alpha$ -position, the halogen atom would be under the joint influence of the carbonyl and carbethoxy-groups, and previous results have established the fact that under these conditions the halogen atom is easily removed by hydrazine and other reducing agents. The product obtained on the bromination of ethyl acetylsuccinate reacted only slightly with hydrazine hydrate, and the volume of liberated nitrogen indicated that the substance was mainly the  $\gamma$ -bromo-compound and contained at most some 18 per cent. of the  $\alpha$ -bromoacetylsuccinate. This result is supported by the work of Ruhemann and Hemmy (T., 1897, 71, 330), who concluded that the product obtained on brominating ethyl acetylsuccinate was the  $\gamma$ -bromo-derivative. The constitution was deduced from a study of the decomposition products resulting from the bromo-ester on distillation under reduced pressure. Ethyl  $\gamma$ -bromo-methylacetoacetate had previously been shown to lose ethyl bromide by the action of heat, forming  $\alpha$ -methyltetronic acid (Roubleff, *Annalen*, 1890, 259, 261; Hantzsch, *ibid.*, 1890, 266, 90; Wolf, *ibid.*, 1895, 288, 11). Ruhemann and Hemmy found that on distillation ethyl bromoacetylsuccinate also lost ethyl bromide and was converted into ethyl  $\omega$ -carboxy- $\alpha$ -methyltetronate, a change which may be expected if the compound has the  $\gamma$ -bromo-structure :

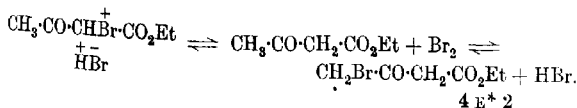


The bromination of ethyl diacetylsuccinate also seems to yield mainly the  $\gamma$ -dibromo-derivative, for on treatment with hydrazine

the nitrogen evolved corresponds with a content of about 21 per cent. of the  $\alpha$ -dibromodiacetylsuccinate. This result is in agreement with the observation of Wolff and Junker (*Annalen*, 1913, 399, 399), who deduced the  $\gamma$ -bromo-structure for the compound from the fact that on heating for some time at 150–160° the ester was converted into bistetronic acid, a change which is readily accounted for by the loss of ethyl bromide:



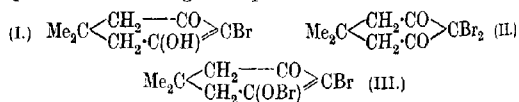
The formation of the  $\gamma$ -bromo-derivatives on the bromination of acetylsuccinic esters is contrary to expectation, inasmuch as it is natural to assume that in the enolisation which precedes bromination the hydrogen atoms would be drawn from the methylene groups between the carbonyl groups, a course which postulates the formation of an  $\alpha$ -bromo-compound. Enolisation may, however, follow a different course and involve a hydrogen atom of the terminal methyl group: in this case, bromination would lead to the formation of the  $\gamma$ -bromo-compound. Brühl (*Ber.*, 1894, 27, 2378; *J. pr. Chem.*, 1894, [ii], 50, 119) has suggested that enolisation of this type may occur, for ethyl diacetylmalonate corresponds in its optical properties with an enol of the formula  $(\text{CH}_2\cdot\text{C}(\text{OH}))_2\text{C}(\text{CO}_2\text{Et})_2$ . Further, Bielecki and Henri (*Compt. rend.*, 1914, 158, 1022) have assigned an abnormal formula, involving such enolisation, to acetylacetone,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ . Auwers and Auffenberg (*Ber.*, 1917, 50, 929) disagree with the enolisations just described, and it is probable that in the acetylsuccinates normal enolisations occur which lead to the formation of the  $\alpha$ -bromo-derivatives. These probably undergo intramolecular change, under the influence of hydrogen bromide, and are converted into the  $\gamma$ -bromo-compounds. In support of this view, it may be pointed out that it has been shown that bromination, in the presence of a halogen acid, is a necessary consequence of the presence of a very electropositive halogen (this vol., p. 894). The migration of the bromine atom from the  $\alpha$ - to the  $\gamma$ -position in the acetyl esters may be expressed as such a reaction, the conversion of ethyl  $\alpha$ -bromoacetoacetate into the  $\gamma$ -compound (Hantzsch, *Ber.*, 1894, 27, 356, 3168; Conrad, *Ber.*, 1896, 29, 1042) taking place according to the scheme



Both reactions may be regarded as reversible, but if the back reaction in the second stage is the slower, the change will result in the accumulation of the  $\gamma$ -bromoacetoacetate. The formation of ethyl  $\gamma$ -bromoacetylsuccinate by the bromination of ethyl acetylsuccinate may be accounted for in a similar way. In this connexion, it is interesting to note that Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 216) has shown that when bromine is passed into ethyl acetoacetate by a rapid current of air, which both introduces the bromine and sweeps out the hydrogen bromide formed, the sole product of the reaction is the  $\alpha$ -bromo-ester.

An alternative explanation of the  $\alpha$ - to  $\gamma$ -bromo-change has recently been put forward (Morgan and Drew, this vol., p. 928) in which it is suggested that the conversion may be accounted for by the transitory formation of a cyclic enolic compound, the terminal methyl group being involved in the enolisation. Smith's observation may be brought into line with this view if it is supposed that hydrogen bromide acts as a catalyst for the change.

The halogen derivatives of *cyclohexane-3:5-dione* have been prepared and studied in some detail by various workers: 4-bromo-*cyclohexane-3:5-dione* by Merling (*Annalen*, 1894, **278**, 42) and a full series of mono- and di-halogen derivatives of 1:1-dimethyl-*cyclohexane-3:5-dione* by Vorländer and Kohlmann (*Annalen*, 1902, **322**, 239). Marked differences in the chemical properties of the mono- and di-halogen derivatives were noted. 4-Bromo-1:1-dimethyl-*cyclohexane-3:5-dione*, for example, is odourless and behaves as a monobasic acid, which readily dissolves in alkali and forms a neutral sodium salt. The bromine atom is very stable, withstanding the action of hot alkali or sodium ethoxide. In this respect, it resembles the monohalogen derivatives of diketohydrindene (Zincke, *Ber.*, 1887, **20**, 1271; 1888, **21**, 293; Roser and Haselhoff, *Annalen*, 1888, **247**, 148). The 4:4-dihalogen derivatives, on the other hand, have a pungent smell and are insoluble in alkali. They act as oxidising agents and liberate iodine from potassium iodide: in addition, one of the halogen atoms is easily removed by the action of alkali or sodium carbonate. Vorländer was of opinion that these differences were not expressed by the ordinary structural formulæ of the compounds, and he proposed the bromoxyl structure (III) to account for the special chemical properties of the dihalogen compounds.



The main idea in adopting the bromoxyl formula was to express

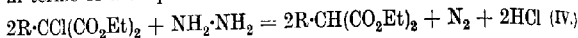
the oxidising properties of the dihalogen compounds, and to differentiate them from substances containing the keto-bromide structure  $\cdot\text{CO}\cdot\text{CBr}_2\cdot\text{CO}\cdot$ , such as the dibromomalononic esters, which he regarded as being without oxidising action. This contention, however, is invalid, for it is now known that the malonic compounds rapidly oxidise hydrazine and hydriodic acid, having this property in common with the dibromo-compounds mentioned above: and it has been further shown (this vol., p. 1109) that the bromoxyl structure does not occur in the malonic series. According to the views expressed by Vorländer, a great number of the compounds described as keto-chlorides and keto-bromides are in all probability organic esters of hypochlorous and hypobromous acid; but there seems to be no weight of evidence in favour of this view, and much can be submitted against it. Norris and Thorpe (T., 1921, 119, 1199) have prepared the chloro- and bromo-derivatives of *cyclohexanespirocyclohexane-3:5-dione* corresponding with the halogen derivatives of 1:1-dimethyl*cyclohexane-3:5-dione* mentioned above; and they find that there is a close resemblance between the chemical properties of the corresponding compounds. The bromoxyl formula is disproved by the preparation of an identical *cyclohexanespiro-4-chloro-4-bromocyclohexane-3:5-dione* both by brominating the 4-chloro-compound and by chlorinating the 4-bromo-compound; similar experiments carried out with 1:1-dimethyl*cyclohexane-3:5-dione* also show that the halogen substitution is confined to the 4-position.

The monohalogen derivatives of the cyclic compounds mentioned above are not acted upon by hydrazine hydrate, and the stability of the halogen atom is doubtless due to the influence of the adjacent double bond, for the absence of reactivity in such cases is well established. The dichloro-derivatives also do not react with hydrazine, and this is in common with the behaviour of 3:3-dichloroacetylacetone and other compounds in which the chlorine atoms are subjected to the influence of two carbonyl groups alone. The dibromo-compounds and the chlorobromo-derivatives, on the contrary, react immediately with hydrazine, and one bromine atom is thereby removed. The reaction is quantitative, and measurement of the liberated nitrogen furnishes a good method of estimation for these compounds.

The examples just referred to fall into line with the cases previously discussed (this vol., p. 1116). Attention was there directed to the fact that, from the point of view of the polarity of the oxygen atoms and the resultant electropositiveness, a chlorine atom should be more stable than a bromine atom; for, on account of its inherently more electronegative nature, the alternate effect results



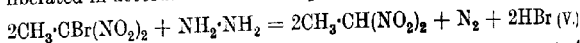
in a less electropositive atom than is the case with bromine under the same structural conditions. The lability of the bromine atom in the compounds referred to above, when contrasted with the stability of the chlorine atom in the corresponding dichloro-derivatives, furnishes striking support for this view. The resistance offered by the chlorine atom to reduction by hydrazine in the cases discussed made it seem of interest to examine the chloro-derivatives of malonic ester. A series of such compounds was examined, and the lower members were found to oxidise hydrazine quantitatively in terms of the equation



Ethyl propylchloromalonate, however, reacts only very slowly, and, even after four hours, less than 50 per cent. reduction is found to have occurred. This result is in agreement with those previously recorded (this vol., p. 904), the steric effect of the substituent group manifesting itself in the higher members of the series.

It is evident that the chloromalonate esters have a greater oxidising power than the dichloro-compounds prepared by Vorländer and by Thorpe, although the former worker regarded them as true keto-chlorides and assigned a bromoxyl formula to the *cyclohexane* derivatives to account for their supposedly greater oxidising powers. The greater reactivity of the chlorine atom in the malonic derivatives seems to be connected with the fact that it is subjected to the influence of the two ethoxyl groups in addition to that of the two carbonyl groups.

As a further example of the labile nature of the halogen atom in the aliphatic nitro-compounds,  $\alpha$ -bromo- $\alpha$ -dinitroethane was examined. It reacts with hydrazine hydrate, nitrogen being quickly liberated in accordance with the equation



It is hoped later to submit spectrographic evidence in support of the keto-bromide structure of the various *cyclohexane* derivatives referred to in this paper.

#### EXPERIMENTAL.

The action of hydrazine on the undermentioned substances took place in a Van Slyke nitrometer. Hydrazine hydrate (50 per cent. solution) was used in all cases, and 1 c.c. furnished sufficient excess for the quantities of halogen compounds used in the experiments.

*Succinchloroimide* was prepared by a modification of Bender's method (Ber., 1886, 19, 2273). A slow stream of chlorine was passed into a solution of succinimide in 15 per cent. sodium hydroxide, the whole being cooled in ice. The chloro-derivative

separated out, and was filtered off, washed with water, and dried on a porous tile. It was thus obtained as a beautiful, white, crystalline substance, m. p.  $149^{\circ}$ . 0.267 Gram, when washed into the nitrometer with a small quantity of alcohol, liberated 24.4 c.c. of nitrogen at  $14^{\circ}$  and 734 mm. The bimolecular quantity therefore liberates 28.15 grams of nitrogen, so the reaction proceeds according to the general equation already given.

*Succinbromimide* was prepared by Lengfeld and Stieglitz's method (*Amer. Chem. J.*, 1893, 15, 215). It is a white, crystalline solid, m. p.  $174^{\circ}$ . 0.356 Gram liberated 24.2 c.c. of nitrogen at  $14^{\circ}$  and 738 mm., so the bimolecular quantity corresponds with 28.08 grams of nitrogen, which is in good agreement with the equation already given.

*1-Chloropiperidine*.—Twelve c.c. of piperidine were gradually added to a well-cooled aqueous solution of sodium hypochlorite containing 2.5 per cent. of available chlorine. After the vigorous reaction ceased, the product was extracted with ether, the extract dried with calcium chloride, and the solvent evaporated off at room temperature under a pressure of 12 mm. The chloropiperidine thus obtained is an oil of 90 per cent. purity: it is very unstable, crystals of piperidine hydrochloride forming in the course of twenty-four hours. 0.1800 Gram, on treatment with hydrazine, liberated 16.2 c.c. of nitrogen at *N.T.P.*, so the sample contained 90.1 per cent. of 1-chloropiperidine.

*Ethyl  $\gamma$ -Bromoacetylsuccinate*.—Acetylsuccinic ester, b. p.  $139^{\circ}/12$  mm., was prepared by the action of the calculated quantity of ethyl chloroacetate on the dry sodium derivative of ethyl acetoacetate. It was brominated by the addition of bromine (1 mol.), in chloroform, to a solution of the ester in the same solvent. The product was washed with water and dilute sodium carbonate solution. After further washing with water, the chloroform solution was dried with anhydrous sodium sulphate, and the solvent removed under greatly reduced pressure. The bromo-compound showed signs of decomposition on distillation, even at a pressure of 8 mm., and in a further preparation distillation was not attempted. The product oxidised hydrazine to a slight extent, 0.590 gram of the ester liberating 4.5 c.c. of nitrogen at  $16^{\circ}$  and 736 mm. This corresponds with 18.5 per cent. of the  $\alpha$ -bromo-compound.

*Ethyl Dibromodiacetylsuccinate*.—The diacetylsuccinate was prepared in the usual way by the action of iodine on ethyl sodioacetoacetate. It was brominated by the gradual addition of bromine (2 mols.), in chloroform, to a solution of the ester in the same solvent. After washing as described in the case above, the chloroform solution was dried with calcium chloride, and the solvent

removed under greatly reduced pressure. The residue was a colourless, viscid syrup which reacted slightly with hydrazine; 2.7 grams were dissolved in 25 c.c. of alcohol, and 10 c.c. of the solution liberated 13.2 c.c. of nitrogen at 16° and 750 mm. This corresponds with 21.2 per cent. of the  $\alpha$ -bromo-compound.

**4-Chloro-1 : 1-dimethylcyclohexane-3 : 5-dione.**—The 1 : 1-dimethylcyclohexane-3 : 5-dione was prepared by the condensation of mesityl oxide\* and ethyl malonate by means of sodium (Vorländer and Erig, *Annalen*, 1897, 294, 314). This was converted into the chloro-compound by the addition of an aqueous solution of sodium hypochlorite to a solution of the parent compound in dilute alkali. On acidifying with hydrochloric acid, the chloro-compound was precipitated, and was crystallised from dilute alcohol. The chloro-compound, m. p. 161°, is not reduced by hydrazine.

**4-Bromo-1 : 1-dimethylcyclohexane-3 : 5-dione** was prepared by the action of bromine on the parent compound (Vorländer and Kohlmann, *loc. cit.*). It is without action on hydrazine.

**4 : 4-Dichloro-1 : 1-dimethylcyclohexane-3 : 5-dione** was prepared by the action of chlorine on an ice-cold solution of the parent substance in chloroform. It was crystallised from dilute alcohol, and found to be unacted upon by hydrazine.

**4 : 4-Dibromo-1 : 1-dimethylcyclohexane-3 : 5-dione** was prepared by triturating the parent compound with the calculated amount of bromine, a little water being present. The product was crystallised from a mixture of equal parts of alcohol and water, and then melted at 144°. It reacted readily with hydrazine, 0.596 gram liberating 23.5 c.c. of nitrogen at 13° and 760 mm. The bimolecular quantity therefore liberates 28.18 grams of nitrogen, one atom of bromine being quantitatively removed in the reaction.

**4-Chloro-4-bromo-1 : 1-dimethylcyclohexane-3 : 5-dione** was prepared by triturating the monochloro-compound with bromine (1 mol.) in the presence of water. It was crystallised from equal parts of alcohol and water, and then melted at 138–139°. It reacted quickly with hydrazine, 0.507 gram liberating 23.6 c.c. of nitrogen at 14° and 755 mm. The bimolecular quantity therefore liberates 28.07 grams of nitrogen, and the bromine atom is quantitatively eliminated in the reduction.

**cycloHexanespiro-4-chloro-** and **cycloHexanespiro-4-bromo-cyclohexane-3 : 5-dione** were prepared by the methods described by Norris and Thorpe (*loc. cit.*). Neither compound reacted with hydrazine. The 4 : 4-dichloro- and the 4 : 4-dibromo-compounds have previously

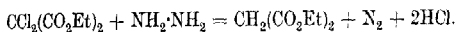
\* We are indebted to Dr. R. C. Menzies for the mesityl oxide used in this preparation. It was prepared by the action of calcium carbide on acetone, and the method proved to be a good one.

been examined (this vol., p. 1116). The former was found to be unacted upon by hydrazine, and one atom of bromine was quantitatively removed from the latter: the cases are thus in agreement with the results now described.

*cycloHexanespiro-4-chloro-4-bromocyclohexane-3:5-dione* was prepared by Norris and Thorpe's method, and was found to react with hydrazine with the ready evolution of nitrogen; 0.587 gram liberated 24.4 c.c. of nitrogen at 13° and 733 mm. The bimolecular quantity therefore liberates 28.19 grams of nitrogen, and the bromine atom is quantitatively removed in the reaction.

*Methyl chloromalonate* was prepared by the gradual addition of sulphuryl chloride (1 mol.) to freshly distilled methyl malonate (1 mol.), the latter being gently warmed to start the reaction. Having been kept for some time, the mixture was heated under reflux for upwards of an hour to complete the reaction, and the product fractionated under reduced pressure; it had b. p. 95°/14 mm. An alcoholic solution was prepared containing 1.665 grams in 25 c.c., and 5 c.c. of this solution, on treatment with hydrazine hydrate, liberated 23.7 c.c. of nitrogen at 14° and 748 mm. The bimolecular quantity therefore liberates 27.86 grams of nitrogen, so the reaction takes place according to equation IV, where R = H.

*Methyl dichloromalonate* was conveniently prepared by the action of a molecular quantity of sulphuryl chloride on the monochloro-ester. After heating under reflux for some time, the mixture was kept over-night and fractionated under reduced pressure. It had b. p. 110°/15 mm. 1.005 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of the solution liberated 23.9 c.c. of nitrogen at 14° and 748 mm. The molecular quantity therefore liberates 28.1 grams of nitrogen, so the reaction is quantitative in terms of the equation



*Ethyl chloroisosuccinate* was prepared by the direct chlorination of *ethyl isosuccinate* (Bischoff, *Annalen*, 1894, **279**, 164). It had b. p. 110°/13 mm. 2.085 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of the solution, on treatment with hydrazine, liberated 24.6 c.c. of nitrogen at 20° and 743 mm. The bimolecular quantity therefore liberates 28.14 grams of nitrogen, so the reaction proceeds in agreement with the equation IV, where R = CH<sub>3</sub>.

*Ethyl ethylchloromalonate* was prepared by direct chlorination of the parent ester. It had b. p. 105°/16 mm. An alcoholic solution was made containing 2.225 grams in 25 c.c., and 5 c.c. of this solution liberated 24.0 c.c. of nitrogen at 16° and 748 mm. The bimolecular quantity therefore liberates 28.02 grams of nitrogen, so the reaction is in accordance with equation IV, where R = C<sub>2</sub>H<sub>5</sub>.

*Ethyl propylchloromalonate* was prepared by the direct chlorination of ethyl propylmalonate. It had b. p.  $125^{\circ}/13$  mm. and  $120^{\circ}/11$  mm. An alcoholic solution was prepared containing 2.365 grams in 25 c.c., and 5 c.c. of this solution had liberated only 11.2 c.c. of nitrogen, or less than half the volume to be expected, after four hours.

$\alpha$ -Bromo- $\alpha$ -dinitroethane was prepared from nitroethane by the following stages, the reactions being carried out in the usual way. Nitroethane  $\rightarrow$   $\alpha$ -bromo- $\alpha$ -nitroethane  $\rightarrow$   $\alpha$ - $\alpha$ -dinitroethane  $\rightarrow$   $\alpha$ -bromo- $\alpha$ -dinitroethane. 1.592 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 23.8 c.c. of nitrogen at  $16^{\circ}$  and 756 mm. The bimolecular quantity therefore liberates 28.1 grams of nitrogen, so the reaction proceeds quantitatively in accordance with equation V.

One of us (E. L. H.) desires to acknowledge his indebtedness to the Carnegie Trust for a grant which enabled him to participate in the work.

CHEMICAL RESEARCH LABORATORY,  
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS. [Received, August 1st, 1922.]

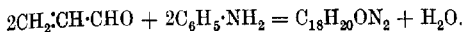
## CCLXI.—*The Interaction of Aniline and Acraldehyde.*

By FREDERICK GEORGE MANN.

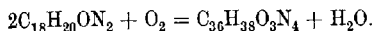
SCHIFF (*Ann. Suppl.*, 1864, **3**, 358) found that aniline and acraldehyde reacted vigorously when mixed, even when chilled in a mixture of ice and salt. After lengthy purification, he obtained an odourless, varnish-like solid, to which he assigned the formula  $C_{18}H_{13}N_2$ , basing this conclusion on the analysis of a platinichloride of the base. Schiff notes that this base gives no crystalline derivatives, and that if an excess of aniline be present the base assumes a beautiful red colour. According to Koenigs (*Ber.*, 1880, **13**, 911), the crude acraldehyde-aniline yields on dry distillation about 7 per cent. of impure quinoline and a small quantity of a less volatile base. He suggested that the yield of quinoline might be increased if the material was distilled with certain metallic oxides; boiling with a mixture of sulphuric acid and potassium chromate, however, gave no quinoline.

In the present investigation, the crude acraldehyde-aniline was prepared by adding aniline to acraldehyde cooled in a mixture of ice and salt; the mixture rapidly yielded a viscous syrup, which changed to a pale yellow solid. This was purified by solution in ether and precipitation with light petroleum, and the white,

amorphous precipitate proved to have the composition  $C_{18}H_{20}ON_2$ , being formed in accordance with the equation



This compound, when fused or exposed in solution, develops a deep red colour owing to oxidation, and not, as Schiff suggested, owing to an excess of aniline in the original preparation; the red oxidation product is separated from the unchanged white base by means of its insolubility in ether. It has the composition  $C_{36}H_{38}O_3N_4$ , and is formed in accordance with the equation



This compound is a deep red, amorphous, feebly basic powder, the colour of which on exposure to light for several weeks slowly fades to pale brown.

Several attempts were made to obtain quinoline from the compound  $C_{18}H_{20}ON_2$ , but none was successful. When slowly heated at atmospheric pressure, the base melts to a red liquid, and aniline in 78 per cent. yield slowly distils; contrary to the statement of Koenigs, no quinoline could be detected in the distillate. Distillation with metallic oxides or prolonged heating with nitrobenzene gave aniline but no quinoline.

*p*-Toluidine reacts with acraldehyde to give the analogous compound,  $C_{20}H_{24}ON_2$ , which on distillation regenerates the base.

#### EXPERIMENTAL.

*The Base  $C_{18}H_{20}ON_2$ .*—Acraldehyde (8.4 grams) was chilled in a mixture of ice and salt and well stirred while 14.0 grams of aniline were slowly added. When about one-third of the aniline had been added, the mixture, which had at first remained a transparent, limpid liquid, suddenly became pale yellow and very viscous, much heat being generated, and finally the complete mixture rapidly solidified. After twenty-four hours, it was dissolved in ether, filtered free from water formed in the condensation, and the dilute solution added slowly to light petroleum (b. p. 60–80°), the base separating as a pure white, amorphous precipitate. If the ethereal solution is too concentrated, the base is precipitated as a viscous syrup, making further treatment difficult. The base was filtered, dried over calcium chloride and paraffin wax until free from petroleum, and, before analysis, heated at 40° in a stream of hydrogen under reduced pressure. On heating, it shrank together into a plastic rod at 70° and melted at 84° [Found: C = 77.2; H = 7.0; N = 10.0; *M*, by cryoscopic method, 566 (in benzene), 550 (in nitrobenzene).  $C_{18}H_{20}ON_2$  requires C = 77.1;

H = 7.2; N = 10.0 per cent.;  $M = 280.2$ ]. The base is freely soluble in ether, chloroform, benzene, or acetone; it dissolves in hot alcohol, and on cooling separates as a white powder. The addition of a small quantity of dilute hydrochloric or sulphuric acid to its acetone solution produces a deep red colour. The following derivatives were prepared.

*Platinichloride*,  $(C_{18}H_{20}ON_2)_2 \cdot H_2PtCl_6$ .—Obtained by filtering a solution of the base in dilute hydrochloric acid directly into chloro-platinic acid solution. The *platinichloride* is a pale buff-coloured powder, which shrinks slightly at  $240^\circ$ , but does not melt below  $300^\circ$ , where it has decomposed to a brittle, black mass (Found: Pt = 20.1.  $C_{36}H_{42}O_2N_4Cl_6Pt$  requires Pt = 20.1 per cent.).

*Picrate*,  $C_{18}H_{20}ON_2 \cdot C_6H_3O_7N_3$ .—Obtained by direct precipitation with alcoholic picric acid solution in the ether-light petroleum filtrate from the original purification of the base. The greenish-brown, amorphous picrate, after purification by reprecipitation in light petroleum, shrank at  $85^\circ$  and melted with decomposition at  $120$ – $121^\circ$  (Found: C = 56.6; H = 4.5; N = 13.5.  $C_{24}H_{23}O_9N_3$  requires C = 56.6; H = 4.5; N = 13.7 per cent.).

*Bromide*.—On adding an excess of a dilute bromine solution in light petroleum to the ether-light petroleum filtrate, a buff-coloured precipitate separated, which evolved hydrogen bromide for several hours. It was then shaken with dilute potassium hydroxide solution and purified by precipitation with light petroleum from chloroform solution. The pale brown, hygroscopic powder shrank at  $110^\circ$  and melted with decomposition at  $178$ – $180^\circ$ ; on exposure to light for three weeks, the colour faded slightly. The composition of the bromide is uncertain, but the base apparently adds on two molecules of bromine and then loses one of hydrogen bromide, giving the compound  $C_{18}H_{19}ON_2Br_3$  (Found: C = 41.6; H = 3.4; Br = 46.8.  $C_{18}H_{19}ON_2Br_3$  requires C = 41.6; H = 3.7; Br = 46.2 per cent.).

*The Oxidation Product*,  $C_{36}H_{33}O_3N_4$ .—The white base is heated for two hours on a water-bath, and the deep red, viscous melt is stirred from time to time. The yield of the oxidation product is increased if a few drops of strong hydrogen peroxide solution are added occasionally. The molten product is allowed to cool in a vacuum over phosphoric oxide, and when cold the brittle red solid is ground to a fine powder and added in small portions at a time to a large excess of anhydrous ether, which is shaken throughout the whole operation. After several minutes' shaking, the residue is filtered and washed free from the deep red filtrate with dry ether. The brick-red powder shrinks at  $126^\circ$  and melts with decomposition at  $143^\circ$  (Found: C = 75.1; H = 6.5; N = 9.8.  $C_{36}H_{33}O_3N_4$

requires C = 75.2; H = 6.7; N = 9.8 per cent.). It gave the following derivatives:

*Platinichloride*,  $C_{36}H_{38}O_3N_4 \cdot H_2PtCl_6$ .—Prepared in the same way as that of the base  $C_{18}H_{20}ON_2$ , but the red compound is so feebly basic that much remained undissolved in dilute hydrochloric acid. The *platinichloride* is a dark red powder which shrinks at  $220^\circ$  and melts with decomposition at  $280^\circ$  (Found: Pt = 19.7.  $C_{36}H_{40}O_3N_4Cl_6Pt$  requires Pt = 19.8 per cent.).

*Picrate*,  $C_{36}H_{38}O_3N_4 \cdot C_6H_3O_7N_3$ .—Precipitated with alcoholic picric acid solution from the saturated ethereal solution of the base. The *picrate* is a dark greenish-brown powder shrinking at  $100^\circ$  and melting to a black mass at  $140^\circ$  (Found: C = 62.5; H = 4.9; N = 12.0.  $C_{42}H_{41}O_{10}N_7$  requires C = 62.7; H = 5.1; N = 12.2 per cent.).

*Bromide*.—Obtained by precipitation in light petroleum-chloroform solution by an excess of a dilute ethereal solution of bromine. The precipitate evolved hydrogen bromide for many hours, and was then treated in the same way as the bromide of the base  $C_{18}H_{20}ON_2$ . The dark reddish-brown powder thus obtained shrank at  $180^\circ$  and melted with decomposition at  $280^\circ$ ; analysis showed it to be an impure tetrabromide.

*Dry Distillation of the Base*  $C_{18}H_{20}ON_2$ .—One hundred and fifty grams of the powdered base were heated gently in an oil-bath. The powder melted to a red liquid which darkened in colour as water and then aniline distilled off. The bath was gradually raised to  $285^\circ$ , when a metal-bath was substituted and the temperature raised to  $450^\circ$ , the complete operation lasting ten hours. Eighty-five grams of damp aniline had then distilled over, and there remained behind 50 grams of light, brittle, carbonaceous matter. Rectification of the distillate gave 78 grams of aniline boiling at  $183$ – $185^\circ$ , which, on acetylation, gave acetanilide, m. p.  $112^\circ$ ; this fraction was followed by about 2 grams of a non-basic liquid in which no quinoline could be detected, and a small, tarry residue remained. The aniline corresponds with a yield of 78.5 per cent.

Aniline also resulted from the distillation of the base under reduced pressure.

Attempts were made to dehydrate the base by mixing it with a large excess of 90 per cent. sulphuric acid and then heating at  $150^\circ$  for three hours; also to oxidise it by adding arsenic acid to such a mixture and heating at  $110^\circ$  for the same period. In each case, the product was diluted, made alkaline, and steam-distilled, but a small yield of aniline alone resulted and much tarry matter remained. Aniline in good yield resulted also from the distillation



of intimate mixtures of the base with lead dioxide and copper oxide, the mixture in each case being distilled from an oil-bath, the temperature of which rose slowly to 250°. When the distillate was refractionated, no quinoline was detected; the addition of the metallic oxides was therefore without effect.

In another experiment, the base was heated under reflux with its own weight of nitrobenzene in an oil-bath, the temperature of which rose from 130° to 190° in the course of six hours. The dark-coloured product was diluted with water, acidified, and the unchanged nitrobenzene distilled with steam; the residue was then made alkaline, and further steam distillation yielded a small quantity of aniline, the greater part of the original base having been converted to a black, tarry mass.

*p-Toluidine and Acraldehyde.*—*p*-Toluidine (8.1 grams) in cold saturated ethereal solution was added to 4.2 grams of chilled acraldehyde, and after twenty-four hours the pale red solution was added to an excess of light petroleum. The cream-coloured, amorphous precipitate shrank at 100° and melted at 111° to a red liquid (Found : C = 77.9; H = 7.5  $C_{20}H_{24}ON_2$  requires C = 77.8; H = 7.8 per cent.).

This base, on dry distillation, gave water and *p*-toluidine, the latter, when dry, melting at 43°.

The author wishes to express his thanks to Professor Sir William Pope, at whose suggestion the work was undertaken. He is indebted to the Department of Scientific and Industrial Research for a grant which enabled the work to be carried out, and to Mr. Fred Flack for much help in the analyses.

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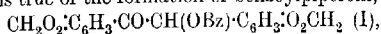
[Received, August 23rd, 1922.]

## CCLXII.—*The Mechanism of the Formation of Benzoylbenzoin by Treatment of Benzoylmandelonitrile with an Alcoholic Solution of Sodium Ethoxide.*

By HERBERT GREENE and ROBERT ROBINSON.

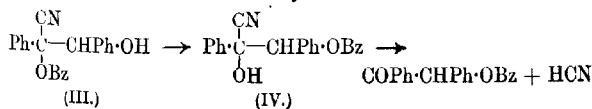
ROBINSON and ROBINSON (P., 1913, 29, 266; T., 1914, 105, 1456) noticed that benzoylmandelonitrile (Francis and Davis, T., 1909, 95, 1404) is converted into benzoylbenzoin together with ethyl benzoate and a little benzyl benzoate when its alcoholic solution is treated with cotarnine, sodium acetate, potassium carbonate or, best of all, with sodium ethoxide, and they expressed the opinion that this result indicates that benzoin-type syntheses are the outcome of

reaction between two molecules of cyanohydrin or benzoylcyanohydrin. The difficulty which was felt in applying Lapworth's view of the mechanism of the benzoin reaction (I., 1903, **83**, 1004) to the production of benzoylbenzoin was in connexion with the elimination of the elements of hydrocyanic acid, which could not in this case be represented as a simple process. This difficulty is removed or rather elucidated by a consideration of the experiments recorded in the present communication, and strong confirmatory evidence of the accuracy of Lapworth's hypothesis has been obtained. If the reaction which leads to the formation of benzoylbenzoin occurs in the first place between two molecules of benzoylmandelonitrile, there is no obvious reason why the yield should be affected by the addition of benzaldehyde. On the other hand, we should expect a material increase if the necessary first stage is the alcoholysis of benzoylmandelonitrile into ethyl benzoate, a cyanide, and benzaldehyde, which last undergoes condensation with a second molecule of benzoylmandelonitrile. We find, however, that the yield of benzoylbenzoin may be considerably increased by the addition of benzaldehyde to the reaction mixture. The same thing is true of the formation of benzoyl-piperoin,

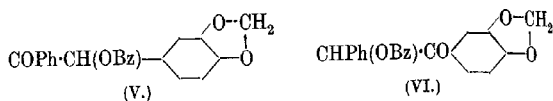


which is best obtained by the action of sodium ethoxide on an alcoholic solution of equimolecular quantities of benzoyl-3:4-methylenedioxymandelonitrile and piperonal. In order to test this point still more stringently, we attempted the condensation of benzoylmandelonitrile and anisaldehyde and found, as we expected, that the main product was a methoxybenzoylbenzoin to which we ascribe the constitution  $\text{COPh}\cdot\text{CH}(\text{OBz})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$  (II) for the reasons which appear in the sequel. It is thus quite clear that the reaction is fundamentally a condensation of benzoylmandelonitrile with benzaldehyde, and the probable aldol-like intermediate stage (III) must then be assumed to lose the elements of hydrocyanic acid with formation of benzoylbenzoin.

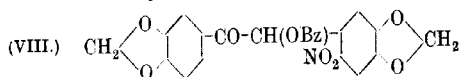
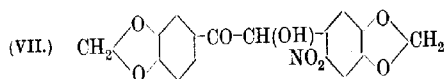
The latter process cannot well be assumed to take place directly so as to give the enol form of the benzoylbenzoin, and the most natural hypothesis is that the benzoyl group wanders and becomes attached to the other oxygen atom. This gives the cyanohydrin (IV) of benzoylbenzoin, and the easy final stage would be the decomposition of this unstable derivative in the strongly alkaline solution, with formation of benzoylbenzoin.



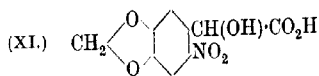
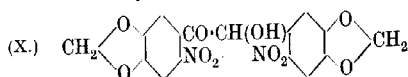
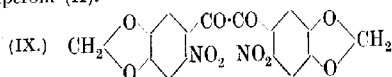
Migrations of an acyl group are of course not at all uncommon, and we have employed the following device in order to prove that the benzoylbenzoin synthesis is a new example of such a molecular rearrangement. By condensing together benzoylmandelonitrile and piperonal on the one hand and benzoylmethylenedioxymandelonitrile and benzaldehyde on the other, we obtained as the main products the isomeric benzoyl derivatives of methylenedioxybenzoin. The isomeride from the first pair melted at  $135^\circ$  and from the second pair at  $148^\circ$  and one of the formulæ V and VI represents the constitution of each of these substances.



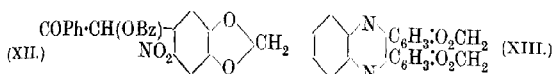
In order to make a definite allotment of these expressions, we have compared the two isomerides in respect of the ease with which they may be nitrated. This method has already been used by G. M. Robinson (T., 1917, **111**, 109) to demonstrate the unsymmetrical character of azoxyveratrole, since it was found that only one nucleus was nitrated or brominated in acetic acid solution. Similarly, we find that piperoin and benzoylpiperoin yield only mononitro-derivatives (VII and VIII, respectively) when nitrated in acetic acid solution, and piperil, it is important to notice, is not attacked under the same conditions.



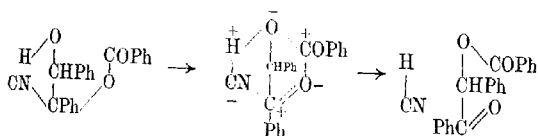
Piperil yields a dinitro-derivative (IX) when treated with concentrated nitric acid, which also converts mononitropiperoin into dinitropiperoin (X).



Further, we find that 3 : 4-methylenedioxymandelic acid yields the nitro-derivative (XI) on nitration in acetic acid solution, whilst homopiperonyl methyl ether is readily nitrated under conditions which do not affect piperonal and piperonyl ethyl ketone. It is abundantly clear, therefore, that V represents a substance which should be capable of nitration in acetic acid solution and under conditions which should leave a substance of formula VI unchanged. The experiment of the nitration of the benzoylmethylenedioxybenzoins gave a conclusive result, since under identical conditions the isomeride melting at  $135^{\circ}$  gave a nitro-derivative melting at  $172^{\circ}$ , and the isomeride melting at  $148^{\circ}$  was recovered unchanged. The nitro-derivative must have the formula XII and therefore the substance melting at  $135^{\circ}$  is represented by V, leaving the expression VI for the isomeride melting at  $148^{\circ}$ .



Now V is obtained from benzoylmandelonitrile and piperonal, and therefore the benzoyl group migrates at some stage of the reaction. It is possible to represent the migration as a process occurring simultaneously with the elimination of the elements of hydrocyanic acid and this is shown below in a scheme which fits into the generalised form of the pinacone-pinacolin and borneol-camphene rearrangements (Robinson, *Mem. Manchester Phil. Soc.*, 1920, 64, iv, 7). The nitrile group is here regarded as a unit analogous to a halogen atom and this is only acceptable if it be assumed to undergo preliminary change to the isonitrile condition. With this proviso, the alternate polarities of the atoms and groups in the rearrangement cycle are well brought out in this example.

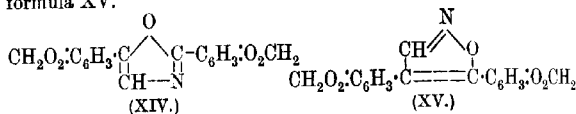


The process is thus represented as continuous, and the benzoyl group is transferred to its new position as the result of the valency distribution changes consequent on the formation of hydrocyanic acid. It makes little difference if the reaction is represented as ionic or if the substance which is eliminated is sodium cyanide, and a similar intermediate stage can be postulated.

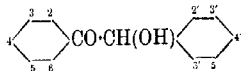
We have not yet attempted the hydrolysis of the benzoates of the mixed benzoins, because the researches of Wren (T., 1909, 95,

1595) on the racemisation phenomena of *l*-benzoin and its methyl ether indicate that it is improbable that pure substances would result. It will probably be necessary to work with substances containing readily removable acyl groups such as the carbomethoxy-derivatives, and it is hoped that investigations in this direction will be made.

The *o*-nitropiperoids now described give interesting results on reduction, but this matter is reserved for a future publication. It should be noted that dinitropiperil (IX) does not condense with *o*-phenylenediamine, and that this is due to the effect of the nitro-groups in the ortho-positions was proved by the ready formation of 2:3-dipiperonylquinoxaline (XIII) from piperil and *o*-phenylenediamine. On one occasion only, the action of sodium ethoxide on an alcoholic solution of benzoylmethylenedioxymandelonitrile resulted in the production of a small amount of a substance,  $C_{17}H_{11}O_5N$ , melting at  $153^\circ$ . This has the composition of a dipiperonyloxazole or isooxazole, but the substance is not identical with 2:5-dipiperonyloxazole (XIV), which was prepared for purposes of comparison by the action of hydrogen chloride on a mixture of piperonal and its cyanohydrin in ethereal solution. Possibly the substance, m. p.  $153^\circ$ , is a dipiperonyl*isooxazole* of the formula XV.



The nomenclature of benzoin derivatives used in this communication is based on the scheme :



## EXPERIMENTAL.

### *Preparation of Benzoylbenzoin.*

A cold solution of sodium ethoxide (from 1.2 grams of sodium) in ethyl alcohol (25 c.c.) was added to a mixture of benzoylmandelonitrile (11.9 grams), ethyl alcohol (30 c.c.), and the weight of benzaldehyde given in the table below. Rise of temperature was checked by cooling the containing vessel in running water, and vigorous shaking was continued until the separation of much solid matter indicated approximate completion of the reaction. Ether (200 c.c.) and water were then added to effect complete solution, and the separated ethereal layer was successively thoroughly washed with

water, aqueous sodium bisulphite, sodium carbonate solution, again with water, and finally dried over anhydrous sodium sulphate. The golden syrup which remained after removal of the solvent slowly deposited crystals which were found to consist essentially of benzoylbenzoin (m. p. 125°) mixed with a little benzoin. The mother-liquor contains ethyl benzoate, and this substance was isolated by distillation in steam, extraction from the distillate, and distillation. The benzoylbenzoin was purified by crystallisation from alcohol, and a further quantity recovered by the addition of water to the sodium sulphate used as drying agent. This portion, having crystallised from ether, was already nearly pure and merely required to be washed with alcohol. The yields obtained are tabulated below and the amounts of benzoylbenzoin quoted should no doubt be increased, as loss is unavoidable in the tedious process of fractionation.

Benzaldehyde employed.	Crude yield.	Benzoylbenzoin.
None	4.4	3.2
2.5 c.c.	6.0	4.2
5.0 c.c. (1 mol.)	7.9	5.7
10.0 c.c.	8.6	6.9

*Benzoylpiperoin* (Formula I).

In our earlier work, some trouble was experienced owing to the fact that benzoylmethylenedioxymandelonitrile could not be crystallised. Subsequently, a crystal nucleus was obtained, and there was then no difficulty in preparing large quantities of the pure substance. It is necessary, however, to describe one experiment with the crude material, since on this occasion a substance was isolated which we have since been unable to produce. The nitrile was prepared as directed by Francis and Davis (*loc. cit.*) and dissolved in ether. The solution was washed with aqueous sodium bisulphite, dried by sodium sulphate, and the solvent evaporated. The residue (27.5 grams) was mixed with a cold solution of sodium ethoxide (from 2.4 grams of sodium) in ethyl alcohol (37 c.c.), when almost at once a stiff paste was produced. This was well stirred during half an hour, and water and ether were then added. A pink solid remained undissolved and was collected and washed with hot water and hot alcohol, which latter solvent removed the colour. The substance was crystallised from acetic acid and proved to be benzoylpiperoin (see below). The separated ethereal solution was washed with water and in the course of a few days deposited some yellow crystals, which were collected (0.8 gram) and crystallised twice from alcohol (Found: C = 65.9, 65.9; H = 3.8, 4.1; N = 4.8, 4.8.  $C_{17}H_{11}O_5N$  requires C = 66.0; H = 3.6; N = 4.5 per cent.). This substance is rather sparingly soluble in alcohol or ether and

crystallises in very thin, pale greenish-yellow flakes melting at  $153^{\circ}$ . Its solution in benzene does not exhibit fluorescence, and in nitric acid it dissolves to a green solution which quickly becomes brown.

The ethereal mother-liquor, after separation of this nitrogenous compound, was evaporated and 0.4 gram of piperoin isolated by crystallisation of the residue from alcohol. The substance melted at  $119-120^{\circ}$ , and at  $120-121^{\circ}$  when mixed with an authentic specimen of piperoin. The yield of pure benzoylpiperoin obtained was very poor (1.1 grams), but was much increased when piperonal was added to the reaction mixture. Thus crude benzoylmethylenedioxymandelonitrile (27.8 grams) and piperonal (15 grams), treated with a solution of sodium ethoxide (from 2.3 grams of sodium) in ethyl alcohol (80 c.c.), gave 11.2 grams of pure benzoylpiperoin.

Benzoylpiperoin crystallises from acetic acid in colourless, diamond-shaped prisms and melts at  $169^{\circ}$  (Found : C = 68.2, 68.3; H = 4.1, 4.0.  $C_{23}H_{16}O_7$  requires C = 68.3; H = 4.0 per cent.). It is very sparingly soluble in ether, alcohol, or acetone, moderately soluble in acetic acid, and readily soluble in chloroform or benzene.

The substance was also obtained from piperoin by prolonged shaking with aqueous sodium hydroxide and benzoyl chloride. The product was crystallised from acetic acid and melted at  $168^{\circ}$ . The melting point was raised to  $168-168.5^{\circ}$  by admixture with a specimen melting at  $169^{\circ}$  prepared as described above.

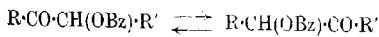
#### 2 : 5-Dipiperonyloxazole (Formula XIV).

The sodium bisulphite compound (27 grams) of piperonal was converted into methylenedioxymandelonitrile by shaking with an aqueous solution of potassium cyanide, and the oil dissolved in ether (200 c.c.). The separated ethereal solution was then dried over anhydrous sodium sulphate, and after the addition of piperonal (15 grams) a stream of hydrogen chloride was passed through the filtered liquid during four and a half hours. The containing vessel was meanwhile cooled in a mixture of ice and salt, and a crystalline precipitate gradually separated. This, which is possibly a hydrochloride, was collected and washed with 90 per cent. alcohol until colourless. The free oxazole thus obtained was crystallised from acetic acid containing a little water and separated in colourless needles melting at  $213^{\circ}$  (Found : C = 65.9; H = 3.8.  $C_{17}H_{11}O_5N$  requires C = 66.0; H = 3.6 per cent.). The substance is readily soluble in acetic acid or hot benzene, moderately soluble in cold benzene, and very sparingly soluble in alcohol. Its benzene and alcoholic solutions exhibit violet fluorescence. It is a feeble base and is converted by concentrated hydrochloric acid to a greenish-yellow,

sparingly soluble hydrochloride, which is hydrolysed by water or alcohol. The strongly fluorescent solution in sulphuric acid slowly acquires a cherry-red colour, which becomes brown and then greenish-brown on gently heating. On the addition of nitric acid to a solution of the substance in acetic acid, a bright yellow liquid is produced and in a few minutes a nitro-derivative separates in canary-yellow needles.

*4'-Methoxybenzoylbenzoin* (Formula II).

A cold solution of sodium ethoxide (from 1.3 grams of sodium) in ethyl alcohol (25 c.c.) was added to a mixture of benzoylmandelonitrile (11.9 grams) and anisaldehyde (11.2 grams) dissolved in ethyl alcohol (30 c.c.). The reaction was controlled by shaking and cooling under the tap during ten minutes and then allowed to proceed at the room temperature for two hours. Water and ether were then added and the ethereal solution washed with water, sodium bisulphite solution, aqueous sodium carbonate, and then again with water. After drying with sodium sulphate, filtering, and distilling off the ether, a syrup remained which was treated with a little methyl alcohol and then deposited crystals (1.4 grams). The substance was collected and twice recrystallised from 90 per cent. alcohol (Found: C = 76.1; H = 5.3.  $C_{22}H_{18}O_4$  requires C = 76.3; H = 5.2 per cent.). This compound is moderately readily soluble in alcohol, sparingly soluble in ether, and melts at 119.5–120.5°. The colourless prisms are seen under the microscope to be of various complex shapes, all of which are possible representatives of the monoclinic type. Attempts to prepare the isomeride of this substance, that is, 4-methoxybenzoylbenzoin, were unsuccessful. In an experiment similar to that described above but starting from benzoyl-*p*-methoxymandelonitrile and benzaldehyde, a substance melting at 105° was isolated in small yield. This was identified as *p*-methoxybenzoin (Meisenheimer, *Annalen*, 1907, **355**, 249), since its melting point was not depressed when the compound was mixed with a specimen of the substance produced by the method of Ekecrantz and Ahlqvist (*Arkiv Kem. Min. Geol.*, 1908, **3**, Nr. 13, 26). In another experiment, the proportion of sodium ethoxide employed was increased by 50 per cent. and in this case a minute amount of 4'-methoxybenzoylbenzoin was isolated. The substance was identified by its melting point, 117–119°, which was raised half a degree by admixture with a specimen melting at 119–120°. The quantity obtained was so small that theoretical conclusions should not, in our opinion, be based on the experiment. It is quite possible that an equilibrium





may be established in an alcoholic solution containing sodium ethoxide, and hydrolysis would naturally occur alongside.

*3' : 4'-Methylenedioxybenzoylbenzoin* (Formula V).

This substance was obtained by condensation of benzoylmandelonitrile (11.9 grams) and piperonal (11.0 grams) in a cold solution of sodium ethoxide (from 1.24 grams of sodium) in alcohol (55 c.c.). The reaction was allowed to proceed during half an hour, and the product isolated as in similar cases already described. The yield of crude product was 10.5 grams and doubtless this material contains a high percentage of methylenedioxybenzoylbenzoin, but its complete purification was difficult and wasteful. Ultimately, by fractional crystallisation from a mixture of ether and light petroleum and by washing the more sparingly soluble fractions with dry ether and finally crystallising from 90 per cent. alcohol, 1.4 grams of the pure substance, melting at  $134-135^{\circ}$ , was obtained (Found: C = 73.4; H = 4.6.  $C_{22}H_{16}O_5$  requires C = 73.3; H = 4.4 per cent.). This substance is sparingly soluble in most organic solvents and crystallises from alcohol in colourless prisms which frequently take the form of hexagonal tablets.

*6'-Nitro-3' : 4'-methylenedioxybenzoylbenzoin* (Formula XII).

*3' : 4'-Methylenedioxybenzoylbenzoin* (1.0 gram) was dissolved in glacial acetic acid (20 c.c.) and, after cooling the containing vessel in melting ice, a mixture of nitric acid (5 c.c.;  $d$  1.42) and acetic acid (5 c.c.) was added. Nitration proceeded under these conditions very slowly and accordingly a further quantity of nitric acid (10 c.c.;  $d$  1.42) was added with vigorous shaking to avoid local concentration. After five minutes, some of the original substance had separated and the flask was removed from the ice-water. The liquid became yellow and then orange, and a clear solution was obtained. After twenty minutes, a pale yellow substance crystallised, and after a further five minutes an equal volume of water was added and the solid collected, washed, and dried (1.1 grams). The substance is readily soluble in hot ethyl acetate, and separates on cooling in pale yellow, dense aggregates of short, prismatic needles melting at  $172^{\circ}$  (Found: C = 65.4; H = 3.8; N = 3.5.  $C_{22}H_{15}O_7N$  requires C = 65.2; H = 3.7; N = 3.5 per cent.). This substance is sparingly soluble in boiling ethyl alcohol, and crystallises from butyl alcohol, in which it is also sparingly soluble, in micaceous, rectangular plates. The interest attaching to the formation of this compound is explained on p. 2185.

## 3 : 4-Methylenedioxybenzoylbenzoin (Formula VI).

This substance was obtained from benzoylmethylenedioxy-mandelonitrile (14.1 grams) and benzaldehyde (10 c.c.) by treatment in the cold with a solution of sodium ethoxide (from 1.2 grams of sodium) in ethyl alcohol (50 c.c.). The product was isolated as in other cases and was purified by crystallisation from acetic acid and from 90 per cent. alcohol. Eventually 2.5 grams of pure substance, melting at 147.5–148.5°, were obtained (Found: C = 73.1; H = 4.4.  $C_{22}H_{16}O_5$  requires C = 73.3; H = 4.4 per cent.).

This compound is sparingly soluble in most solvents and separates from alcohol in small octahedra which have four triangular and four quadrilateral faces. A mixture of equal parts of this substance and of the isomeride, melting at 134–135°, melted at 120°. The nitration of this substance was attempted under conditions identical with those described above for its isomeride, the experiments being carried out side by side. No reaction occurred, and the substance was recovered entirely unchanged, as was proved by crystallisation of the product and determinations of melting point, alone and mixed with the original specimen.

## 6'-Nitropiperoin (Formula VII).

A large number of experiments were carried out in the hope of increasing the yield of piperoin obtained from piperonal, but although some variations gave good results the improvements were not consistently observed. The original process of F. M. Perkin (T., 1891, 59, 164) appears to be the best and we are able to confirm the experience of this author that the yields are materially decreased when quantities of piperonal greater than 5 grams are employed. The potassium cyanide used should be the purest available. Nitration of piperoin can readily be effected in stages, and the mononitro-derivative was obtained by operating under the following conditions. A mixture of nitric acid (30 c.c.;  $d$  1.42) and glacial acetic acid (30 c.c.) was added with shaking to finely powdered piperoin (6.2 grams) suspended in acetic acid (30 c.c.). The containing vessel was cooled in running water at 6°, and a crystalline substance gradually separated from the clear yellow solution. After an hour, water was added, the solid collected and crystallised from alcohol, 3.9 grams of pure substance being obtained. In another experiment, carried out at 0° but otherwise under similar conditions, 4.0 grams of piperoin gave 2.9 grams of the crystallised nitropiperoin. In this case, the crude product was well washed with water and a little hot alcohol and then crystallised from ethyl acetate (Found: C = 56.0; H = 3.2; N = 4.2.  $C_{16}H_{11}O_5N$  requires C = 55.7; H = 3.2; N = 4.1 per cent.). The substance

separates from ethyl alcohol and ethyl acetate in hexagonal, prismatic needles which are pale lemon-yellow when freshly prepared but rapidly become intense yellow on exposure to light. Decomposition ensues on heating, but if the determination be carried out rapidly the compound melts at approximately  $166^{\circ}$ . It is very sparingly soluble in chloroform or ether, sparingly soluble in benzene, and moderately soluble in ethyl alcohol, acetic acid, or acetone. When the crude substance, obtained as described above from 4.5 grams of piperoin, was distilled in a current of steam, 0.2 gram of nitromethylenedioxybenzene crystallised from the distillate and in the condenser. This was collected and crystallised from methyl alcohol and found to melt at  $148^{\circ}$ , alone or mixed with an authentic specimen which had been obtained as a by-product in the nitration of piperonal.

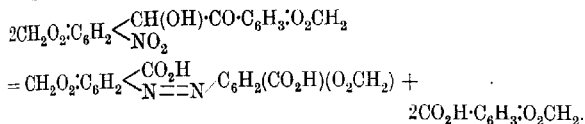
*6'-Nitro-3 : 4 : 3' : 4'-dimethylenetetraoxybenzoylpiperoin*  
(Formula VIII).

Benzoylpiperoin (2 grams) was dissolved in warm acetic acid (10 c.c.) and, after cooling, a mixture of nitric acid (5 c.c.;  $d$  1.42) and acetic acid (5 c.c.) was at once added. The solution became yellow and was kept at the temperature of tap water during an hour, after which it was poured into water, and the precipitate collected and washed. The crude material was dissolved in a large volume of methyl alcohol and, on long standing, a yellow, crystalline crust separated. This was washed with hot alcohol and the substance then recrystallised twice from ethyl acetate (Found: C = 61.2; H = 3.7.  $C_{23}H_{15}O_9N$  requires C = 61.5; H = 3.3 per cent.). Nitrobenzoylpiperoin is sparingly soluble in most organic solvents and crystallises in slender, pale yellow needles melting at  $160.5-161.5^{\circ}$ .

*6 : 6'-Dinitropiperoin* (Formula X).

This substance has been prepared by the further nitration of nitropiperoin by means of nitric acid ( $d$  1.42), but it is more economical to nitrate piperoin directly in the following manner. Finely powdered piperoin (5 grams) was gradually added to nitric acid (200 c.c.;  $d$  1.42), cooled to  $5^{\circ}$ , and mechanically stirred. After one hour, the mixture was added to water, and the precipitate collected, washed with hot alcohol (50 c.c.) and hot ethyl acetate (100 c.c.), and crystallised from acetic acid. The yield was 3.2 grams, and some mononitropiperoin could be recovered from the ethyl acetate extract. Dinitropiperoin is almost colourless when pure, and separates from acetic acid in highly characteristic, double fishtail crystals and nodular bundles of these. On heating, it decomposes, becoming yellow to light brown at  $150-160^{\circ}$ , brown at  $170^{\circ}$ ,

dark brown at 210°, and black at 240° (Found: C = 48.8, 49.6; H = 3.0, 2.7; N = 7.1.  $C_{16}H_{10}O_{10}N_2$  requires C = 49.2; H = 2.6; N = 7.2 per cent.). The substance is very sparingly soluble in benzene, chloroform, ether, or alcohol, sparingly soluble in ethyl acetate, but moderately readily soluble in acetone. A boiling nitrobenzene solution of nitropiperoin or of dinitropiperoin gradually becomes orange-red, and after long boiling a brick-red acid substance separates on cooling the solution. This dissolves in sulphuric acid to a most intense royal blue solution and on warming with nitric acid is converted to a bright red compound which crystallises from nitrobenzene in brittle needles melting with decomposition at 305° and at the same temperature when mixed with a specimen of 6:6'-dinitro-3:4:3':4'-di(methylenedioxy)azobenzene (Robinson and Robinson, T., 1915, **107**, 1753). The reaction therefore leads to the production of di(methylenedioxy)azobenzenedicarboxylic acid, and is quite analogous to the similar decomposition of nitro-methylenedioxy mandelic acid. In the case of mononitropiperoin, the process occurs in all probability in accordance with the equation:



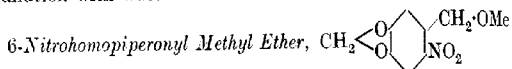
6:6'-Dinitropiperil (Formula IX).

Piperil (7.5 grams) was added to nitric acid (200 c.c.; *d* 1.42) at 5°, and the mixture continuously stirred. After an hour and a half, the product was isolated and extracted with benzene to remove unchanged piperil. This was again nitrated, and ultimately the yield of the dinitro-derivative amounted to 6.0 grams. Even after four hours some unchanged piperil could be isolated by extraction with hot benzene, and the insoluble residue was crystallised from a mixture of nitrobenzene and butyl alcohol (Found: C = 49.7; H = 2.4; N = 7.2.  $C_{16}H_8O_{10}N_2$  requires C = 49.5; H = 2.1; N = 7.2 per cent.). This substance crystallises in golden-yellow needles which gradually decompose above 200°. It is very sparingly soluble in most organic solvents, but is readily soluble in hot nitrobenzene. It does not react with *o*-phenylenediamine in boiling acetic acid solution. A suspension in glacial acetic acid was heated at 100° and aqueous hydrogen peroxide added. A considerable quantity of the material passed into solution; after filtration, the acetic acid was removed by distillation in steam, and the aqueous solution filtered and concentrated. On cooling, 6-nitropiperonylic acid separated in yellow needles and after recrystallisation melted

at 171–172° and at the same temperature when mixed with a specimen obtained by the hydrolysis of methyl 6-nitropiperonylate.

2 : 3-Dipiperonylquinoxaline (Formula XIII).

A mixture of piperil (2.7 grams), *o*-phenylenediamine (1.3 grams), sodium acetate (2.0 grams), and glacial acetic acid (25 c.c.) was boiled during ten minutes. On cooling, the red solution deposited greenish-yellow crystals, and after recrystallisation from acetic acid the amount obtained was 2.8 grams. In another experiment, the sodium acetate was omitted and this did not affect the result materially. The substance crystallises from acetic acid in well-shaped, hexagonal tablets which are yellow by reflected light and pale green by transmitted light. It melts at 204° (Found : C = 71.4; H = 4.1; N = 7.6.  $C_{22}H_{14}O_4N_2$  requires C = 71.4; H = 3.8; N = 7.6 per cent.). Dipiperonylquinoxaline is very sparingly soluble in acetone, ether, or hot methyl or ethyl alcohol, moderately soluble in ethyl acetate, and in benzene to a solution exhibiting violet fluorescence. It also dissolves in hot chloroform and separates on cooling in rhombic prisms. It dissolves in concentrated sulphuric acid to an intense indigo-blue solution which becomes red on dilution with water.



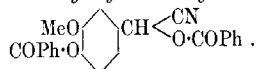
Homopiperonyl methyl ether was obtained in almost theoretical amount when a molecular proportion of sodium methoxide, dissolved in absolute methyl alcohol, was carefully added with cooling to homopiperonyl bromide (Robinson and Robinson, T., 1914, 105, 1463), dissolved in methyl alcohol. When the temperature no longer tended to rise, the methyl alcohol was distilled, the residue dissolved in ether, and the extract washed with water and dried with calcium chloride. The substance was purified by distillation and obtained as a colourless oil boiling constantly at 127°/22 mm. (Found : C = 64.9; H = 6.0.  $C_9H_{10}O_3$  requires C = 65.1; H = 6.0 per cent.). When this ether was added to a 10 per cent. solution of nitric acid (*d* 1.42) in acetic acid, it was quantitatively nitrated in a few minutes at the ordinary temperature. The product was isolated by pouring into water, filtration, and crystallisation from ethyl alcohol (Found : C = 51.5; H = 4.5; N = 6.7.  $C_9H_9O_3N$  requires C = 51.2; H = 4.3; N = 6.6 per cent.). This substance is somewhat sparingly soluble in most organic solvents and crystallises in silky, golden-yellow needles melting at 114.5–115.5°.

Some further observations on the nitration of piperonyl derivatives may be quoted. Piperonal and piperonyl ethyl ketone (Foulds

and Robinson, T., 1914, **103**, 1963) are practically unaffected by a 10 per cent. solution of nitric acid in acetic acid after a treatment five times as long as that which suffices to effect the nitration described above. Methyl piperonylacetate,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , is very readily nitrated in acetic acid solution and with formation of the 6-nitro-derivative,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , which may also be obtained by the esterification of 6-nitropiperonylacetic acid (Foulds and Robinson, *loc. cit.*) with methyl-alcoholic sulphuric acid. Prepared in either way, *methyl 6-nitropiperonylacetate* crystallises from methyl alcohol in pale yellow needles melting at  $105^\circ$  (Found: N = 5.9.  $\text{C}_{10}\text{H}_9\text{O}_6\text{N}$  requires N = 5.8 per cent.).

Piperil is not changed by treatment during an hour with nitric acid and acetic acid in the proportions used for the nitration of 3':4'-methylenedioxybenzoylbenzoin, but methylenedioxymandelic acid is rapidly converted by such a mixture into the 6-nitro-derivative, which melts at  $181\text{--}183^\circ$  with decomposition and previous darkening. The substance showed the characteristic reactions described by Robinson and Robinson (*loc. cit.*).

*Benzoyl-3-benzoyloxy-4-methoxymandelonitrile,*



This substance was obtained by shaking an ice-cold aqueous solution of vanillin (1 mol.), potassium hydroxide (1 mol.), and potassium cyanide (1.1 mols.) with benzoyl chloride (2 mols.). The solid was collected, washed with water, and crystallised from alcohol. The substance separated in colourless octahedra melting at  $143\text{--}148^\circ$  (Found: C = 71.0; H = 4.5.  $\text{C}_{23}\text{H}_{17}\text{O}_5\text{N}$  requires C = 71.3; H = 4.4 per cent.). Attempts to convert this rather sparingly soluble substance into a benzoin derivative were unsuccessful.

Table of colour reactions in concentrated sulphuric acid.

Name or formula of substance.	Colour change.	
	In cold reagent.	On heating.
Anisoin	Yellow-green	Reddish-purple.
Piperoin	Reddish-brown	Mole gray.
I		
II	Colourless $\rightarrow$ greenish-blue	Olive-green.
V	Dark green $\rightarrow$ reddish-brown	Dark brown.
VI	Yellow $\rightarrow$ green $\rightarrow$ brown	Reddish-brown $\rightarrow$ reddish-purple.
VII	Reddish-brown	Purplish-black $\rightarrow$ reddish-purple $\rightarrow$ sienna.
VIII	Yellow $\rightarrow$ greenish-brown $\rightarrow$ purplish-black	Reddish-purple $\rightarrow$ gray.
LX	Claret	Pale yellow.
X		
XII	Blood-red	Carmin $\rightarrow$ brown.

One of us (H. G.) desires to express his thanks to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.

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CCLXIII.—*Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. Part II. The s-Tetra-substituted Amides of Bromo- and Chloro-malonic Acid.*

By RALPH WINTON WEST.

IN Part I (Backes, West, and Whiteley, T., 1921, **119**, 359), a description was afforded of the investigation of the action of bromine on the *s*-disubstituted amides of malonic acid. The work has been extended to include the *s*-tetra-substituted amides, in which it has been found that substitution of bromine for hydrogen in chloroform or acetic acid solution only takes place in the methylene group of the malonyl radicle. This is in contrast to the behaviour of such compounds as malonanilide and malontoluidide, in which substitution of bromine also takes place in the aromatic nucleus.

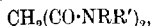
During the attempts at exhaustive bromination of bromomalonomethylanilide and bromomalontetraphenylamide, these substances were exposed to the action of bromine vapour for several days at the ordinary temperature. In each case an unstable orange-red substance was obtained, which had the general characteristics of perbromides of the type mentioned by Fries (*Ber.*, 1904, **37**, 2338; *Annalen*, 1906, **346**, 128). These compounds, on boiling with ethyl alcohol, gave colourless solutions which deposited sparingly soluble solids having the constitution of bromomalonomethylbromoanilide and bromomalontetrbromophenylamide, respectively. Further treatment with the halogen resulted in decomposition of the product under consideration.

This limitation of the halogenation of the benzene nucleus to the mono-substituted derivative in cases where the phenyl group is attached to tertiary nitrogen is in accord with the results obtained by Fries and other workers on the problem of the bromination of the aromatic bases.

The substitution of halogen for the hydrogen atoms of the methylene group in this series of compounds has furnished phenomena which, whilst not of true "steric hindrance" character, must

nevertheless be included under the more general heading of "strain interference."

As the groups R and R' of a substituted malonamide,



where R and R' represent alkyl and aryl radicles or hydrogen, are varied, so the behaviour of the hydrogen atoms of the methylene group towards halogens is affected. This can be explained by supposing that the displacement of these hydrogen atoms is governed by a factor which may be termed the "strain value" of the compound. This "strain value" could vary from a magnitude allowing the formation of perfectly stable di-halogenated derivatives to one prohibiting the formation of any stable halogen compound. If "potential strain values" are assumed for the bromine and chlorine atoms, the stability of the halogenated compound would be determined by the resulting strain between the residue of the compound and the halogen atom. That this strain cannot be wholly due to volume steric relationships is suggested by the fact that, although bromine and chlorine have atomic volumes of much the same order, there is a wide difference between their action. This is well illustrated by the results obtained in the case of the substituted malonamides.

Value of the group NRR'.	Action of bromine.	Action of chlorine.
(1) $\text{NH}_2$	Both mono- and di-bromo-compounds can be isolated, but there is a tendency to proceed directly to the latter.	Only the dichloro-compound can be obtained by direct chlorination.
(2) $\text{NHMe}$	Both mono- and di-bromo-compounds can readily be prepared.	As in (1).
(3) $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$	As in (2).	The monochloro-compound can be isolated.
(4) $\text{N}(\text{CH}_2\text{Ph})_2$	Forms a mono-bromo-compound only.	Forms both mono- and di-chloro-compounds.
(5) $\text{NMePh}$	As in (4).	Forms a monochloro-compound only.
(6) $\text{NPh}_2$	As in (4).	As in (5).

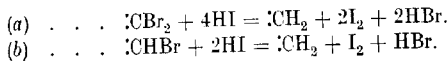
A consideration of results (1) to (4) would lead to the belief that bromine has twice the "potential strain value" of chlorine, but results (5) and (6) suggest that the two halogens have equal values. It seems, therefore, that, in this respect, the relative "strain values" of bromine and chlorine must be greater than 1, but less than 2. This allows a monobromo-compound to exist under a state of strain too great to permit the formation of a dichloro-compound. In order to test this supposition, the action of excess of chlorine on a number of bromo-compounds was investigated.



Group NRR'.	Compound formed by the action of chlorine on :	
	Monobromo-derivative.	Dibromo-derivative.
(1) NHMe	Chlorobromo-.	Chlorobromo-.
(2) NHEt	As in (1).	As in (1).
(3) NH·C <sub>6</sub> H <sub>4</sub> Br	"	"
(4) N(CH <sub>3</sub> Ph) <sub>2</sub>	Dichloro-.	"
(5) NMePh	Monochloro-.	"
(6) NPh <sub>2</sub>	"	"

From all the foregoing it will be seen that in the combinations (1) to (3) the strain in the linking of the second bromine atom is such that this atom is readily replaced by chlorine, whilst the bromine of the monobromo-compounds is quite stable towards this reagent. In (4) it is probable that under the influence of the chlorine an unstable substance of the chlorobromo-type is first formed, and is then transformed into the dichloro-derivative. In cases (5) and (6) the strained bromo-compounds at once give place to the chloro-analogues.

Interesting confirmation of this strain supposition is furnished by the action of hydrogen iodide on these substances under the conditions laid down in Part I of this paper. The reaction in the case of the bromo-compounds proceeds readily according to the equations



Although in combinations (1), (2), and (3) the chlorine is not reactive either in the chlorobromo- or the dichloro-derivatives, yet in (4) the chlorine of the dichloro-compound is slowly reactive, and in (5) and (6) quantitative reduction of the chloro-derivative takes place within a reasonable period at the ordinary temperature. This must mean that in these last two substances the chlorine atom exists under similar conditions of strain as does the bromine atom in the monobromo-derivatives of types (1) and (2).

This problem differs essentially from ordinary "steric hindrance" inasmuch as the halogen atom which is most difficult to insert is the one most easily removed. In its basic principles, the explanation put forward in this paper resembles that suggested by Chattaway and Harrison (T., 1916, 109, 171) to explain the reactivity of one nitro-group in tetranitromethane and of the bromine atom in bromotritnitromethane.

The labile nature of the halogen atoms in the malonamides is being fully investigated by the reaction velocity methods, and the mechanism of the reactions of this class of compounds with hydrogen iodide and other reagents will be discussed in a future paper.

## EXPERIMENTAL.

*Malonmethylanilide.*

*Bromomalonmethylanilide*,  $\text{CHBr}(\text{CO}\cdot\text{NMePh})_2$ .—Malonmethylanilide (3.5 grams; 1 mol.), dissolved in chloroform, was treated with 6.5 c.c. of a 10 per cent. (by volume) solution of bromine in the same solvent (1 mol.). After the solvent had evaporated, the residual syrup was rendered solid by treatment with 5 c.c. of dry ether. The yield was 3.7 grams. *Bromomalonmethylanilide* is readily soluble in chloroform or acetic acid, and is sparingly soluble in ethyl alcohol, benzene, carbon tetrachloride, or ether. It crystallises from a mixture of chloroform and alcohol as stout, colourless prisms, m. p.  $198^\circ$  [Found: Br(total) = 22.20; Br(malonyl) = 22.19.  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}_2\text{Br}$  requires Br = 22.14 per cent.]. By the action of excess of chlorine on this compound, chloromalonmethylanilide is obtained.

*Bromomalonmethylobromoanilide*,  $\text{CHBr}(\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Br})_2$ .—Finely powdered bromomalonmethylanilide was kept in an atmosphere of bromine for seven days. A softly-crystalline, red substance was obtained, which behaved like a perbromide of the type described by Fries (*loc. cit.*). On boiling this compound with ethyl alcohol, in which it dissolved very readily, sparingly soluble crystals separated out. *Bromomalonmethylobromoanilide* is sparingly soluble in organic solvents; it crystallises from ethyl alcohol in stout, colourless prisms, m. p.  $172^\circ$  [Found: Br(total) = 46.59; Br(malonyl) = 15.07.  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2\text{Br}_3$  requires Br(total) = 46.23; Br(malonyl) = 15.41 per cent.].

*Chloromalonmethylanilide*,  $\text{CHCl}(\text{CO}\cdot\text{NMePh})_2$ .—Five grams of malonmethylanilide, dissolved in chloroform, were treated with a solution of chlorine in the same solvent (1 mol.). After the solvent had evaporated, the residue (5.5 grams) was crystallised from ethyl alcohol, from which it separated in colourless prisms, m. p.  $187^\circ$  (Found: Cl = 11.34.  $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}_2\text{Cl}$  requires Cl = 11.20 per cent.).

Solutions of both bromine and chlorine are without further action on this compound.

*Malontetraphenylamide.*

*Bromomalontetraphenylamide*,  $\text{CHBr}(\text{CO}\cdot\text{NPh}_2)_2$ , is prepared similarly to bromomalonmethylanilide by direct bromination of malontetraphenylamide in chloroform solution. The yield is nearly theoretical. *Bromomalontetraphenylamide* is readily soluble in chloroform or acetic acid, and sparingly soluble in ethyl alcohol, toluene, or carbon tetrachloride. It crystallises from toluene in

colourless prisms, m. p.  $201^{\circ}$  [Found: Br(total) = 16.62; Br(malonyl) = 16.20.  $C_{27}H_{21}O_2N_2Br$  requires Br = 16.48 per cent.].

By the action of excess of chlorine on this compound chloro-malontetraphenylamide is obtained.

*Bromomalontetra-bromophenylamide*,  $CHBr[CO \cdot N(C_6H_4Br)_2]_2$ , is obtained by the prolonged action of bromine vapour on bromo-malontetraphenylamide, the conditions of formation being similar to those obtaining in the preparation of bromomalonmethylbromo-anilide. *Bromomalontetra-bromophenylamide* is readily soluble in chloroform or acetic acid, but is sparingly soluble in all other solvents. It crystallises from a mixture of chloroform and ethyl alcohol in small, colourless needles, m. p.  $169^{\circ}$  [Found: Br(total) = 50.15; Br(malonyl) = 10.00.  $C_{27}H_{17}O_2N_2Br_5$  requires Br(total) = 49.92; Br(malonyl) = 9.98 per cent.].

*Chloromalontetraphenylamide*,  $CHCl(CO \cdot NPh_2)_2$ , is prepared similarly to chloromalonmethylanilide by the action of chlorine in chloroform solution on malontetraphenylamide. The yield is nearly theoretical. *Chloromalontetraphenylamide* is very soluble in chloroform or acetic acid, readily soluble in ethyl alcohol or benzene, and sparingly soluble in ether or the ligroids. It crystallises from ethyl-alcoholic solution in colourless prisms, m. p.  $204^{\circ}$  [Found: Cl = 8.18.  $C_{27}H_{21}O_2N_2Cl$  requires Cl = 8.05 per cent.].

Solutions of both bromine and chlorine are without further action on this compound.

#### *Malontetrabenzylamide.*

*Bromomalontetrabenzylamide*,  $CHBr[CO \cdot N(CH_2Ph)_2]_2$ .—One gram of malontetrabenzylamide, dissolved in chloroform, was treated with 1.1 c.c. of a 10 per cent. solution of bromine in the same solvent (1 mol.). The solvent was allowed to evaporate, and the residual oil rendered solid by treatment with dilute sodium carbonate solution. *Bromomalontetrabenzylamide* crystallises from ethyl-alcoholic solution in colourless prisms, m. p.  $137^{\circ}$  [Found: Br(total) = 14.59; Br(malonyl) = 14.85.  $C_{31}H_{29}O_2N_2Br$  requires Br = 14.77 per cent.].

By the action of excess of chlorine on this compound, dichloro-malontetrabenzylamide is obtained.

*Chloromalontetrabenzylamide*,  $CHCl[CO \cdot N(CH_2Ph)_2]_2$ , is prepared similarly to chloromalonmethylanilide by the action of chlorine in chloroform solution on malontetrabenzylamide. From ethyl alcohol the chloromalontetrabenzylamide crystallises in small needles, m. p.  $119^{\circ}$  [Found: Cl = 7.29.  $C_{31}H_{29}O_2N_2Cl$  requires Cl = 7.14 per cent.].

Bromine in solution is without action on this compound, but excess of chlorine converts it into the dichloro-compound.

*Dichloromalontetrazbenzylamide*,  $\text{CCl}_2[\text{CO}\cdot\text{N}(\text{CH}_2\text{Ph})_2]_2$ , is formed by the action of excess of chlorine in chloroform solution on malon-tetrazbenzylamide. It crystallises from ethyl alcohol as colourless prisms, m. p.  $138^\circ$  (Found:  $\text{Cl} = 13.11$ .  $\text{C}_{31}\text{H}_{28}\text{O}_2\text{N}_2\text{Cl}_2$  requires  $\text{Cl} = 13.35$  per cent.).

Solutions of both bromine and chlorine are without further action on this compound.

#### *Malon-p-bromoanilide.*

*Chloromalon-p-bromoanilide*,  $\text{CHCl}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , is readily prepared by the action of chlorine (1 mol.) in acetic acid solution on malon-*p*-bromoanilide. It is readily soluble in acetone or acetic acid, and sparingly soluble in all other ordinary organic solvents. It crystallises from acetic acid solution in colourless, thin prisms, m. p.  $239^\circ$  (Found:  $\text{Cl} = 7.98$ ;  $\text{Br} = 35.97$ .  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}_2\text{ClBr}_2$  requires  $\text{Cl} = 7.94$ ;  $\text{Br} = 35.81$  per cent.). A solution containing one molecule of bromine reacts with this compound to form chlorobromomalon-*p*-bromoanilide, whilst chlorine similarly yields dichloromalon-*p*-bromoanilide.

*Dichloromalon-p-bromoanilide*,  $\text{CCl}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , is readily prepared from malon-*p*-bromoanilide by the action of chlorine (2 mols.) in chloroform solution. It is sparingly soluble in all ordinary organic solvents except acetic acid, from which it crystallises in colourless needles, m. p.  $184^\circ$  (Found:  $\text{Cl} = 14.67$ ;  $\text{Br} = 33.07$ .  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{Cl}_2\text{Br}_2$  requires  $\text{Cl} = 14.75$ ;  $\text{Br} = 33.25$  per cent.).

*Chlorobromomalon-p-bromoanilide*,  $\text{CClBr}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , may be prepared by the action of chlorine on either bromomalon- or dibromomalon-*p*-bromoanilide. It is readily soluble in ethyl alcohol, chloroform, acetic acid, or benzene, and crystallises from ethyl alcohol in colourless prisms, m. p.  $162^\circ$  [Found:  $\text{Cl} = 6.75$ ;  $\text{Br}(\text{total}) = 45.62$ ;  $\text{Br}(\text{malonyl}) = 15.38$ .  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{ClBr}_3$  requires  $\text{Cl} = 6.75$ ;  $\text{Br}(\text{total}) = 45.65$ ;  $\text{Br}(\text{malonyl}) = 15.22$  per cent.].

#### *Malondiethylamide.*

*Chlorobromomalondiethylamide*,  $\text{CClBr}(\text{CO}\cdot\text{NH}\cdot\text{Et})_2$ , is readily prepared by the action of chlorine in chloroform solution on bromo- or dibromo-malondiethylamide. It is readily soluble in acetone, acetic acid, chloroform, ethyl alcohol, or benzene, and crystallises from the last-named solvent in colourless needles, m. p.  $122^\circ$  (Found:  $\text{Cl} = 13.27$ ;  $\text{Br} = 29.91$ .  $\text{C}_7\text{H}_{12}\text{O}_2\text{N}_2\text{ClBr}$  requires  $\text{Cl} = 13.07$ ;  $\text{Br} = 29.45$  per cent.).

*Malondimethylamide.*

*Dichloromalondimethylamide*,  $\text{CCl}_2(\text{CO}\cdot\text{NHMe})_2$ , is obtained when malondimethylamide in solution is acted upon by a solution of chlorine or alkaline hypochlorite. If one molecule of the chlorinating agent is used, a mixture is obtained of the dichloro-compound and unchanged malondimethylamide. *Dichloromalondimethylamide* is readily soluble in water, acetic acid, ethyl alcohol, chloroform, or acetone, and sparingly soluble in benzene, carbon tetrachloride, or ether. It crystallises from a mixture of ethyl alcohol and benzene in colourless needles, m. p.  $158^\circ$  (Found : Cl = 35.58.  $\text{C}_5\text{H}_8\text{O}_2\text{N}_2\text{Cl}_2$  requires Cl = 35.65 per cent.).

*Chlorobromomalondimethylamide*,  $\text{CClBr}(\text{CO}\cdot\text{NHMe})_2$ , is prepared similarly to chlorobromomalondimethylamide, which it closely resembles as to solubility. It crystallises from benzene in colourless prisms, m. p.  $130^\circ$  (Found : Cl = 14.71; Br = 33.12.  $\text{C}_5\text{H}_8\text{O}_2\text{N}_2\text{ClBr}$  requires Cl = 14.57; Br = 32.83 per cent.). The chlorine in this compound is not reactive towards hydrogen iodide; an estimation of the malonyl halogen gave Br = 32.95 per cent.

I desire to express my sincere thanks to Assistant-Professor M. A. Whiteley for the help and encouragement given throughout the conduct of this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

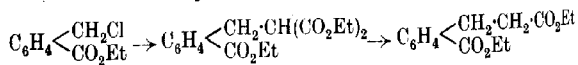
SOUTH KENSINGTON, S.W.7.

[Received, August 2nd, 1922.]

# CCLXIV.—*The Chlorination and Bromination of the Toluic Acids and the Preparation of the Phthalaldehydic Acids.*

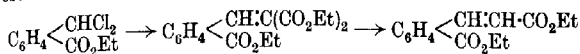
By WILLIAM DAVIES and WILLIAM HENRY PERKIN, jun.

DURING the course of an investigation on ring formation which is in progress, it became necessary to devise methods by means of which *o*-, *m*-, and *p*-derivatives with varying side chains and especially esters of the type  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{[CH}_2\text{]}_x\cdot\text{CO}_2\text{Et} \\ \text{[CH}_2\text{]}_y\cdot\text{CO}_2\text{Et} \end{smallmatrix}$  could be readily prepared and in quantity. It seemed probable that certain substances of this type might be obtainable from  $\omega$ -halogen derivatives of the toluic esters by the usual malonic ester synthesis, thus

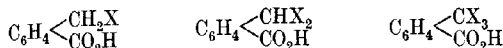


The  $\omega$ -dichloro-derivatives of these esters might also prove

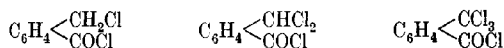
valuable, since they might serve for the synthesis of unsaturated esters corresponding with the type represented above :



With the view of testing reactions such as these, we made a study of the literature and were surprised to find that, whilst the  $\omega$ -halogen derivatives of the xylenes have been carefully studied, little is known of the  $\omega$ -halogen derivatives of the toluic acids of the general formulæ



Salkind (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 508) has studied the action of bromine on the boiling solution of *p*-toluic acid in bromoform, by which means he obtained  $\omega$ -bromo-*p*-toluic acid,  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Br}$ ; he also prepared  $\omega$ -bromo-*o*-toluic acid from phthalide by heating with bromine in a sealed tube, but these methods have restricted application and are obviously unsuitable for the preparation of the  $\omega$ -halogenotoluic acids in quantity. During the course of a long series of experiments on halogen substitution in the  $\omega$ -position in the toluic acids, we have found that substances of this kind and their derivatives may be readily prepared by the following simple series of reactions. The toluic acid is first converted into the acid chloride,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ , by the action of thionyl chloride, and this is then treated with chlorine or bromine at temperatures varying from 160—240° according to the degree of substitution desired. Substances of the type

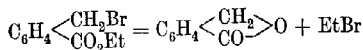


are produced in this way in very good yield. Careful treatment with formic acid converts the acid chlorides into the free substituted toluic acids, and derivatives of these acids, such as esters and amides, are readily obtained from the acid chlorides by the action of alcohols, ammonia, etc. In this way we have prepared a large number of interesting  $\omega$ -halogen derivatives of the three, *o*-, *m*-, and *p*-, toluic acids, and as the conditions of preparation and details of physical properties are given in full in the experimental section of this communication, they need not be stated here, but attention may be directed to certain interesting points which have arisen during the course of this investigation.

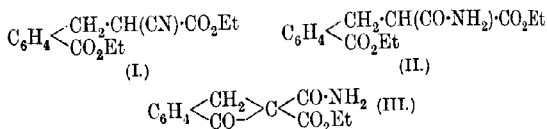
When *o*-toluoyl chloride is treated with bromine at 185°, it does not yield the  $\omega$ -bromo-acid chloride as might have been expected, but the hydrogen bromide formed during the bromination of the

methyl group reacts with the group  $\text{-COCl}$ , and the product consists apparently entirely of  $\omega$ -bromo-*o*-toluoyl bromide,  $\text{C}_6\text{H}_4(\text{COBr})\cdot\text{CH}_2\text{Br}$ . Cases analogous to this have already been described by Aschan (*Ber.*, 1912, **45**, 1913; 1913, **46**, 2162) and by Staudinger and Anthes (*Ber.*, 1913, **46**, 1417).

Ethyl  $\omega$ -bromo-*o*-toluate is decomposed, on heating, into ethyl bromide and phthalide,



and as the decomposition proceeds smoothly, it furnishes a very convenient method for the preparation of phthalide. This ready elimination of ethyl bromide does not appear to take place under other conditions, thus, for example, the bromo-ester reacts normally when digested in acetone solution with sodium iodide, yielding ethyl  $\omega$ -iodo-*o*-toluate,  $\text{C}_6\text{H}_4(\text{CO}_2\text{Et})\cdot\text{CH}_2\text{I}$  (m. p.  $32\cdot5^\circ$ ), and potassium cyanide converts it into the nitrile of homophthalic acid,  $\text{C}_6\text{H}_4(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CN}$ . Ethyl  $\omega$ -bromo-*o*-toluate also reacts readily with the sodium derivative of ethyl cyanoacetate to form ethyl  $\alpha$ -cyano-*o*-carbethoxy- $\beta$ -phenylpropionate (I), and this is decomposed by concentrated sulphuric acid with the formation of the corresponding imide (II) and not of the hydrindone derivative (III).



The investigation of the  $\omega$ -dichlorotoluoyl chlorides,



obtained by the action of chlorine on the toluoyl chlorides at a final temperature of  $210^\circ$ , has given interesting results. These substances exhibit remarkable stability and may be distilled with very little decomposition at the ordinary pressure. *o*-, *m*-, and *p*- $\omega$ -Dichlorotoluoyl chlorides are crystalline substances and melt at  $28^\circ$ ,  $49^\circ$ , and  $45^\circ$ , respectively. On treatment with alcohol, they yield the  $\omega$ -dichlorotoluic esters, of which the *o*- and *m*-isomerides are colourless liquids, whereas the *p*-derivative crystallises and melts at  $46^\circ$ .

When *o*-, *m*-, and *p*- $\omega$ -dichlorotoluoyl chlorides are warmed with formic acid, they yield the corresponding *o*-, *m*-, and *p*- $\omega$ -dichlorotoluic acids, which crystallise readily and melt at  $155^\circ$ ,  $132^\circ$ , and  $158^\circ$ , respectively.

One of the most valuable uses of the  $\omega$ -dichlorotoluoyl chlorides

has resulted from the discovery that they serve as a very convenient source of the phthalaldehydic acids,  $C_6H_4(CO_2H) \cdot CHO$ .

The methods available up to the present for the preparation of these important acids are so tedious and unsatisfactory that their investigation and especially their employment for synthetical processes, for which they are particularly well adapted, becomes a very serious matter.

The most readily prepared of these acids is *o*-phthalaldehydic acid (m. p.  $100.5^\circ$ ), which may be obtained from phthalonic acid by heating with sodium bisulphite or aniline. In order to prepare the *m*- and *p*-phthalaldehydic acids, Reinglass (*Ber.*, 1891, 24, 2423) converted the *m*- and *p*-toluonitriles into the corresponding cyanobenzyl chlorides,  $CH_2Cl \cdot C_6H_4 \cdot CN$ , by chlorination at  $150^\circ$ . When these substances are boiled with aqueous copper nitrate, they yield the cyanobenzaldehydes,  $CHO \cdot C_6H_4 \cdot CN$ , from which the phthalaldehydic acids,  $CHO \cdot C_6H_4 \cdot CO_2H$ , may be obtained by boiling with concentrated hydrochloric acid. We have repeated this process and find it most laborious and unsatisfactory; moreover, the *m*- and *p*-phthalaldehydic acids thus obtained are difficult to purify, owing to the presence of considerable quantities of the corresponding phthalic acids. This is evidenced by the low analytical figures given by Reinglass and by the fact that this investigator gives the melting points of *m*- and *p*-phthalaldehydic acids as  $165^\circ$  and  $285^\circ$ , whereas in reality these acids melt at  $175^\circ$  and  $250^\circ$ , respectively. Simonis (*Ber.*, 1912, 45, 1584) has prepared the phthalaldehydic acids by heating the phthalaldehydes with bromine in a sealed tube, and although we can substantiate his claim that yields of 50–60 per cent. may be obtained in this way, the process is of little value as a method of preparation, partly because the aldehydo-acids thus formed are contaminated by the corresponding phthalic acids, which makes them difficult to purify, and partly because the phthalaldehydes are very inaccessible substances. A method for the ready preparation particularly of the *m*- and *p*-aldehydic-acids was therefore very desirable, and we have found that these acids may be conveniently prepared from the corresponding *m*- and *p*-toluic acids by converting them into the dichlorotoluoyl chlorides and then simply digesting these with milk of lime or chalk in an inert atmosphere:



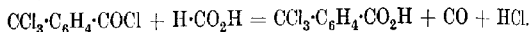
The phthalaldehydic acids produced in this way in excellent yield, are almost free from the corresponding phthalic acids and therefore are readily obtained pure by one crystallisation; the melting points observed by us have been stated above. These experiments,



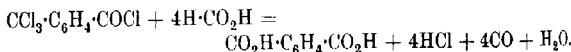
in the carrying out of which we were fortunate in having the assistance of Mr. Herbert Clayton, indicate that the method employed with such success in the case of the phthalaldehydic acids will be found to be applicable to the preparation of other aldehydo-acids at present unknown or difficult of access, and investigations in this direction are in progress.

*o-, m-, and p- $\omega$ -Trichlorotoluic Acids and their Derivatives.*

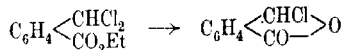
When the toluoyl chlorides are chlorinated at an initial temperature of  $160^{\circ}$ , gradually rising to  $240^{\circ}$ , they are converted into the corresponding  $\omega$ -trichlorotoluoyl chlorides,  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ . The *m*- and *p*-isomerides distil at  $287^{\circ}$  and  $296^{\circ}$ , respectively, and have not yet been obtained crystalline. The *o*-compound distils at about  $145\text{--}155^{\circ}/20$  mm. and deposits crystals melting at  $87^{\circ}$ . These acid chlorides are readily decomposed by boiling with alcohol, yielding the  $\omega$ -trichloro-*p*-toluic esters,  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , and the corresponding acids are obtained from the chlorides by the action of anhydrous formic acid :



In carrying out this decomposition, it is essential to determine carefully the lowest temperature (varying from  $45\text{--}85^{\circ}$  in the different cases) at which the formic acid interacts, and the trichloro-acids are then readily obtained in a state of purity. These interesting acids crystallise well from benzene or chloroform, the *o*-, *m*-, and *p*-isomerides melting, respectively, at  $141\text{--}144^{\circ}$ ,  $142^{\circ}$ , and  $197^{\circ}$ . If, however, the trichlorotoluoyl chlorides are boiled with formic acid, the group  $-\text{CCl}_3$  becomes converted into carboxyl and the corresponding phthalic acids result :



Interesting decompositions have been observed in the case of  $\omega$ -dichloro-*o*-toluic ester and  $\omega$ -trichloro-*o*-toluic ester. When  $\omega$ -dichloro-*o*-toluic ester is heated, it behaves like  $\omega$ -bromo-*o*-toluic ester (p. 2211) and yields  $\alpha$ -chlorophthalide with loss of ethyl chloride:

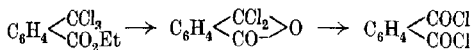


The substance thus produced melts at  $60\text{--}61^{\circ}$  and is evidently identical with the  $\alpha$ -chlorophthalide obtained by Gabriel (*Ber.*, 1916, 49, 1612) from *o*-phthalaldehydic acid by the action of thionyl chloride. A somewhat similar change takes place when  $\omega$ -trichloro-*o*-toluic ester is heated.

At its boiling point, this ester decomposes with elimination of

ethyl chloride, and the substance which distils at 277°/758 mm. solidifies, melts at about 12°, and evidently consists of *s*-phthalyl chloride,  $C_6H_4(COCl)_2$ , which has m. p. 15–16° and b. p. 276°/760 mm.

Probably *as*-phthalyl chloride (dichlorophthalide) is first produced and then at the temperature of the decomposition or of the distillation undergoes isomeric change and is converted into the symmetrical modification (compare Ott, *Annalen*, 1912, **392**, 275) :



#### EXPERIMENTAL.

##### *Derivatives of o-Toluic Acid.*

*ω*-Bromo-*o*-toluoyl Bromide,  $COBr \cdot C_6H_4 \cdot CH_2Br$ .—The *o*-toluoyl chloride required in this preparation is obtained in a yield of 95 per cent. by boiling *o*-toluic acid with thionyl chloride (10 per cent. excess of 1 mol.) and distils at 213°/760 mm. In carrying out the bromination, bromine (15.5 c.c.; 2 atoms) is slowly dropped into the acid chloride (46.35 grams; 1 mol.) at 185–195°, the orifice of the dropping funnel being placed well below the surface of the acid chloride in order to allow the bromine and hydrogen bromide produced to react with as little loss as possible. The reaction proceeds very smoothly and is complete in an hour. On repeatedly distilling the product under 32 mm., the bromo-acid bromide was readily obtained pure in a yield of 65–67 per cent. of that theoretically possible. Bromo-*o*-toluoyl bromide boils at 170–171°/32 mm. and crystallises in clusters of colourless needles which melt at 33–34° (Found: C = 34.3; H = 2.2; Br = 57.0.  $C_8H_6OBr_2$  requires C = 34.5; H = 2.2; Br = 57.6 per cent.).

*Ethyl ω*-Bromo-*o*-toluate,  $CH_2Br \cdot C_6H_4 \cdot CO_2Et$ .—This ester is readily prepared by slowly adding melted *ω*-bromo-*o*-toluoyl bromide (91 grams) to absolute alcohol (150 c.c.), the whole being well shaken and cooled in ice. After remaining over-night, the product is poured into water, the bromo-ester extracted with ether, the ethereal solution well washed with water and sodium carbonate, dried over sodium sulphate, and the ether removed. Ethyl *ω*-bromo-*o*-toluate is a colourless, heavy oil which becomes yellow on keeping and does not solidify at 0° (Found: Br = 34.2.  $C_{10}H_{11}O_2Br$  requires Br = 32.9 per cent.). It possesses a pungent and yet rather pleasant odour and is lachrymatory when hot. It is difficult to obtain this ester in a perfectly pure state because, on attempted distillation at 30 mm., it readily suffers decomposition with elimination of ethyl bromide and formation of a white solid

melting at  $73^{\circ}$ . This substance was identified by its properties, analysis, and by the method of mixed melting points, as phthalide (Found: C = 71.5; H = 4.6. Calc., C = 71.6; H = 4.5 per cent.).

The yield of phthalide is almost quantitative and this substance is conveniently prepared by boiling the bromo-ester in a test-tube for about five minutes, when, on cooling, the contents solidify to almost pure phthalide. When ethyl  $\omega$ -bromo-*o*-toluate is allowed to stand with cold aqueous alcoholic ammonia for several days, colourless needles are obtained melting at  $150^{\circ}$  and this substance was recognised as phthalimidine from its analysis (Found: N = 10.9. Calc., N = 10.5 per cent.), its solubility in acids, and from the properties of the nitroso-derivative (m. p.  $157^{\circ}$ ), which agree in all respects with those of nitrosophthalimidine (Graebe, *Ber.*, 1884, 17, 2599).

*Ethyl  $\omega$ -Iodo-*o*-toluate*,  $\text{CH}_2\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ .—For the preparation of this ester, sodium iodide (19 grams) was dissolved in acetone (150 c.c.), and the well-cooled solution mixed with ethyl  $\omega$ -bromo-*o*-toluate (24.3 grams) in acetone (25 c.c.), when the liquid became brown, heat was evolved, and a white precipitate of sodium bromide rapidly separated. After remaining at the ordinary temperature for two hours, the acetone was removed by gently warming under reduced pressure, the residue extracted with ether, most of the ether distilled off, and the brownish-red residue kept at the ordinary temperature, when a mass of pale brown needles gradually separated. After filtering from a small amount of oil and pressing on porous porcelain, a 70 per cent. yield of the iodo-ester was obtained in faintly yellow needles which became colourless on washing with sodium bisulphite solution. *Ethyl  $\omega$ -iodo-*o*-toluate* consists of minute, colourless needles melting at  $32.5^{\circ}$ , which become yellow and ultimately brown on long keeping (Found: I = 44.2.  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{I}$  requires I = 43.8 per cent.). It is very soluble in most organic solvents, is slightly lachrymatory in the cold and much more so when warmed. Like the corresponding bromo-derivative, it does not appear to react smoothly with magnesium, but this point is being further investigated.

*Preparation of Ethyl Homophthalate*,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}$ .—This ester is readily obtained in the following manner. Ethyl  $\omega$ -bromo-*o*-toluate, prepared from 100 grams of  $\omega$ -bromo-*o*-toluoyl bromide in the way described above, was dissolved in absolute alcohol (300 c.c.) containing finely powdered potassium cyanide (32 grams) in suspension. The mixture was boiled for eight hours on the water-bath, half the alcohol distilled off, the reaction product kept over-night, and the brown liquid filtered from the potas-

ium salts. Dry hydrogen chloride was passed into the filtrate, during which crystals of ammonium chloride began to separate even in the cold. When saturated with hydrogen chloride, the solution was boiled, two-thirds of the alcohol then distilled off under reduced pressure, the residual solid matter removed by filtration, washed with a little alcohol, and the filtrate poured into water.

The oil which separated was extracted with ether, the ethereal solution washed with sodium carbonate, dried over sodium sulphate, and the ether removed. The residual liquid (58 grams) was distilled under reduced pressure, when a considerable amount of low-boiling ester passed over at first, but 34 grams (40 per cent. of theory) were obtained boiling at 172–177°/33 mm. The presence of phthalide, which is somewhat soluble in hot but sparingly soluble in cold water, could not be detected by extracting the ester with boiling water. On redistillation, the ethyl homophthalate boiled at 176°/33 mm. and with trifling decomposition at 293° under the ordinary pressure. It agreed in this and other properties with the ethyl homophthalate described by Gabriel (*Ber.*, 1887, **20**, 2500). The yield of ester obtained under these conditions is not so large as was expected, but further experiments will be made in the hope of improving it.

*The Action of Ethyl  $\omega$ -Bromo-o-toluate on Ethyl Sodiocynoacetate.*

The great reactivity of the halogen atom in ethyl  $\omega$ -bromo-o-toluate made it desirable at this stage to ascertain whether the substance could be induced to react with sodium derivatives in the usual way and without the elimination of ethyl bromide and formation of phthalide.

The sodium derivative of ethyl cyanoacetate was chosen for this purpose because it seemed likely that the products would be solid and therefore readily purified. Ethyl  $\omega$ -bromo-o-toluate (24.3 grams; 1 mol.) was carefully added to the solution of ethyl sodiocynoacetate, prepared from ethyl cyanoacetate (11.3 grams; 1 mol.) and sodium ethoxide (from 2.3 grams of sodium in 100 c.c. of absolute alcohol). Decomposition occurred at once, heat was developed, and sodium bromide separated. The whole was heated on the water-bath for half an hour, most of the alcohol removed by distillation, the residue mixed with water, and the oil extracted with ether. The ethereal solution was washed with water, dried over sodium sulphate, and the ether removed, when an oil (20 grams) remained. On distillation under 16 mm., unchanged ethyl cyanoacetate first passed over and then two fractions, b. p. 195–225° (8 grams) and 280–282° (3 grams), were collected. The higher fraction, which is probably the condensation product of two mole-

cules of ethyl  $\omega$ -bromo-*o*-toluate with one molecule of ethyl cyanoacetate, did not crystallise on cooling at  $-10^{\circ}$  or keeping at room temperature for six months and was not further examined. The other fraction was redistilled under the same pressure, and the portion boiling at  $210$ — $220^{\circ}$  (5 grams) then slowly solidified. Ethyl  $\alpha$ -cyano-*o*-carbethoxy- $\beta$ -phenylpropionate is readily soluble in most organic solvents, but crystallises from light petroleum in colourless needles melting at  $38$ — $40^{\circ}$  (Found : N = 5.2.  $C_{15}H_{17}O_4N$  requires N = 5.1 per cent.). It dissolves readily in cold concentrated sulphuric acid with the evolution of some heat, and the solution, after remaining for twenty-four hours and then pouring into water, deposits crystals of ethyl *o*-carbethoxybenzylmalonamic acid. This characteristic substance separates from dilute alcohol in glistening needles and melts at  $132^{\circ}$  (Found : C = 61.5; H = 6.8; N = 4.9.  $C_{15}H_{16}O_5N$  requires C = 61.4; H = 6.5; N = 4.8 per cent.).

*$\omega$ -Bromo-*m*-toluoyl Bromide and Ethyl  $\omega$ -Bromo-*m*-toluate.*

$\omega$ -Bromo-*m*-toluoyl bromide was obtained from *m*-toluoyl chloride exactly in the way described in the preparation of the *o*-isomeride (p. 2207). The yield of the pure bromide was only 50 per cent. of theory, a comparatively complex mixture being formed. It boils at  $167^{\circ}/22$  mm. and solidifies at room temperature (Found : Br = 57.8.  $C_8H_7OBr_2$  requires Br = 57.6 per cent.). Ethyl  $\omega$ -bromo-*m*-toluate, prepared from the bromide by the action of alcohol in the usual way, boils at  $174$ — $176^{\circ}/30$  mm. without decomposition and possesses a peculiar sour odour (compare Salkind and Ssamenov, *loc. cit.*).

*The  $\omega$ -Dichlorotoluic Acids and their Derivatives.*

The methods of preparation of the  $\omega$ -dichlorotoluoyl chlorides and of the corresponding dichlorotoluic acids are almost identical in all three cases and may be briefly summarised as follows. The toluoyl chloride is chlorinated, under anhydrous conditions, in bright light, the temperature being initially at  $160^{\circ}$  and towards the end of the reaction at  $210^{\circ}$  (thermometer in the liquid), until the increase of weight corresponds with the introduction of two atoms of chlorine. The absorption of chlorine, which is rapid at first, slows down, but by gradually raising the temperature, action can be continued at a satisfactory rate, thus, for example, 40 grams of toluoyl chloride can be dichlorinated in this way in three hours. The product is distilled under ordinary or under diminished pressure and an 80 per cent. yield of the dichlorotoluoyl chloride, boiling within two degrees, is obtained. The lowest fraction of the distillate consists of a mixture of mono- and di-chlorotoluoyl chlorides, and the higher fraction of di- and tri-chlorotoluoyl chlorides.

The corresponding esters are obtained by pouring the acid chlorides into excess of alcohol, shaking until reaction has taken place, and finally heating on the steam-bath. After standing over-night, the alcoholic solution is poured into water, the ester, if a liquid, dissolved in ether, washed with sodium carbonate, and worked up in the usual way.

In the preparation of the  $\omega$ -dichlorotoluic acids, the corresponding acid chloride is mixed with about six times its weight of anhydrous formic acid, and the mixture gradually warmed until the acid chloride begins to dissolve. The whole is maintained at this temperature until complete solution has taken place, the time usually required for the preparation of 2 grams of the acid being from one to four minutes, and during the reaction carbon monoxide and hydrogen chloride are evolved.

It is essential to carry out the decomposition at the lowest possible temperature, because, if this is materially exceeded, considerable hydrolysis of the chlorine atoms in the side chain may occur.

When the product is cooled, the acid separates in a crystalline condition and can generally be obtained pure by crystallisation from chloroform or benzene.

$\omega$ -Dichloro-*o*-toluoyl chloride crystallises in thick, glassy prisms, melts at  $27-28^\circ$ , and distils at  $151/22$  mm. or  $267-269/740$  mm. (Found: Cl = 47.7.  $C_8H_5OCl_2$  requires Cl = 47.6 per cent.).

$\omega$ -Dichloro-*o*-toluic acid, obtained by the action of formic acid on  $\omega$ -dichloro-*o*-toluoyl chloride at  $63^\circ$ , is very soluble in hot, but only slightly soluble in cold, benzene or formic acid, and crystallises from these solvents in colourless, glistening needles melting at  $155^\circ$  (Found: C = 47.1; H = 3.2.  $C_8H_5O_2Cl_2$  requires C = 46.8; H = 2.9 per cent.). The amide of  $\omega$ -dichloro-*o*-toluic acid is formed by passing dry ammonia into a cold benzene solution of the acid chloride until no more ammonium chloride separates, filtering hot, and concentrating the benzene solution. On cooling, the acid amide separates in glistening, colourless prisms melting at  $117^\circ$  (Found: N = 6.9.  $C_8H_7ONCl_2$  requires N = 6.9 per cent.). When heated at  $140^\circ$ , hydrogen chloride and a black tar are produced, and hydrogen chloride is also eliminated by boiling with water or with pyridine. The examination of the interesting products of these reactions is contemplated.

Ethyl  $\omega$ -dichloro-*o*-toluate is a colourless, mobile liquid with a pungent and yet distinctly pleasant, fruity odour (Found: C = 51.0; H = 4.2.  $C_{10}H_{13}O_2Cl_2$  requires C = 51.5; H = 4.3 per cent.). It boils without decomposition at  $172/42$  mm. and can be rapidly distilled under the ordinary pressure. When slowly boiled under the ordinary pressure, a steady stream of ethyl chloride is pro-

duced and in about fifteen minutes 10 grams of the substance will have become converted into a brown oil which, when kept for twenty-four hours in a desiccator, solidifies to a mass of crystals. These were collected, pressed on porous porcelain, and crystallised from benzene, when a good yield of  $\alpha$ -chlorophthalide was obtained in colourless plates melting at  $60-61^\circ$  (compare Gabriel, *Ber.*, 1916, 49, 1608).

*o*-Dichloro-*m*-toluoyl chloride crystallises in long, colourless needles, melts at  $48-49^\circ$ , and distils at  $280-282^\circ/765$  mm. *o*-Dichloro-*m*-toluic acid, prepared from this chloride by the action of formic acid at  $75^\circ$ , is very soluble in chloroform or benzene, from which it separates in microscopic prisms melting at  $132^\circ$  (Found: C = 47.0; H = 2.9.  $C_8H_6O_2Cl_2$  requires C = 46.8; H = 2.9 per cent.). Ethyl *o*-dichloro-*m*-toluate is a colourless liquid closely\*resembling the corresponding *o*-isomeride.

*o*-Dichloro-*p*-toluoyl chloride forms minute, colourless needles melting to a clear liquid at  $44-45^\circ$  and distilling at  $285-286^\circ/745$  mm. (Found: Cl = 47.4. Calc., Cl = 47.6 per cent.). Wegscheider and Suida (*Monatsh.*, 1912, 33, 1026) record the melting point  $50-52^\circ$ , but their specimen was far from pure, for it did not melt to a clear liquid and the percentage of chlorine found was more than 3 per cent. too low.

*o*-Dichloro-*p*-toluic acid, obtained from the acid chloride by the action of formic acid at  $70-75^\circ$ , is difficult to obtain pure. It crystallises from formic acid, in which it is sparingly soluble, in small needles and from benzene, in which it is readily soluble, in short, thick prisms, and melts at  $151-158^\circ$  (Found: C = 46.0; H = 3.0.  $C_8H_6O_2Cl_2$  requires C = 46.8; H = 2.9 per cent.). Ethyl *o*-dichloro-*p*-toluate consists of small, thin prisms melting at  $45-46^\circ$  and possessing a faint, pleasant odour.

#### *The o*-Trichlorotoluic Acids and their Derivatives.

The *o*-trichlorotoluoyl chlorides are prepared by the continued chlorination of the toluoyl chlorides (p. 2206). As chlorination proceeds, the temperature of the liquid must be gradually raised from  $160^\circ$  to  $240^\circ$  and even at this high temperature the introduction of the third atom of chlorine into the side chain is very slow. About ten hours' heating is required for the preparation of 70 grams of an *o*-trichlorotoluoyl chloride.

*o*-Trichloro-*o*-toluoyl Chloride.—The chlorinated product did not boil constantly, nearly half distilling at  $275-285^\circ$  and about half at  $285-288^\circ$  under 758 mm. pressure. The latter fraction is an oil possessing the usual properties of aromatic acid chlorides (Found: Cl = 54.1.  $C_8H_4OCl_3$  requires Cl = 55.0 per cent.).

It is probable that this specimen was contaminated with traces of  $\omega$ -dichloro-*o*-toluoyl chloride, which is difficult to remove completely by fractional distillation. When, however, fractionation was repeatedly carried out under diminished pressure, considerable quantities of an oil were obtained which distilled at 145–155°/20 mm. and, on cooling, deposited crystals which, after recrystallisation from light petroleum, melted at 87° and consisted of pure  $\omega$ -trichloro-*o*-toluoyl chloride. This substance was proved by a mixed melting-point determination to be identical with the phthalic acid tetrachloride (m. p. 88°) which Vongerichten (*Ber.*, 1880, 13, 447) obtained, along with an isomeride melting at 47°, from phthalide by the action of phosphorus pentachloride. *Ethyl*  $\omega$ -trichloro-*o*-toluate, prepared in the usual way, is a colourless, mobile liquid with a rather pleasant, faint odour. It is difficult to obtain this ester in a pure state, for some decomposition occurs when distillation under diminished pressure is attempted. On boiling the ester (7 grams) at the ordinary pressure, ethyl chloride was eliminated, the decomposition being complete in about five minutes and, on cooling, a few colourless crystals of phthalic anhydride separated, formed no doubt as the result of the presence of moisture. The liquid portion of the product fumed in moist air like an acid chloride, boiled almost completely at 276–277°/758 mm., and the pale yellow distillate solidified at 0° and melted at about 12°. These properties indicate that this substance is a fairly pure specimen of *s*-phthalyl chloride,  $C_6H_4(COCl)_2$ , which has m. p. 15–16° and b. p. 276.7°/760 mm., whereas the constants for *as*-phthalyl chloride  $C_6H_4<\overset{Cl}{\underset{Cl}{C}}O>O$ , are m. p. 88–89° and b. p. 275.2°/719.8 mm. (Ott, *Annalen*, 1912, 392, 275).

$\omega$ -Trichloro-*o*-toluic acid, prepared from  $\omega$ -trichloro-*o*-toluoyl chloride by the action of formic acid at 45–55°, crystallises from benzene in needles melting at 141–144°. The melted acid decomposes slowly with evolution of hydrogen chloride, and therefore the melting point varies somewhat with the rate of heating (Found: C = 40.6; H = 2.2.  $C_8H_5O_2Cl_3$  requires C = 40.1; H = 2.1 per cent.).

$\omega$ -Trichloro-*m*-toluoyl chloride, obtained in excellent yield in the usual manner (p. 2212), is a colourless oil boiling at 287°/754 mm. It is readily hydrolysed by boiling sodium hydroxide solution with the formation of *isophthalic* acid, which was identified by conversion into the dimethyl ester melting at 64°. *Methyl*  $\omega$ -trichloro-*m*-toluate, prepared from the acid chloride and methyl alcohol, is conveniently recrystallised by dissolving in cold acetone, in which it is very readily soluble, and then adding dilute methyl alcohol



until a milkiness is produced. The methyl ester, which has a faint pleasant odour, separates in colourless needles melting at  $55^{\circ}$  (Found: C = 42.2; H = 2.9.  $C_9H_7O_2Cl_3$  requires C = 42.6; H = 2.8 per cent.). *o*-Trichloro-*m*-toluic acid, prepared by the action of formic acid on the acid chloride at  $70-75^{\circ}$ , is sparingly soluble in formic acid, but readily so in chloroform or benzene, and crystallises in sparkling laminae melting at  $142^{\circ}$  (Found: C = 39.8; H = 2.2.  $C_8H_5O_2Cl_3$  requires C = 40.1; H = 2.1 per cent.).

*o*-Trichloro-*p*-toluoyl chloride is a colourless oil distilling at  $296^{\circ}/756$  mm. with trifling decomposition. *o*-Trichloro-*p*-toluic acid, prepared from the acid chloride by the action of formic acid at  $80-85^{\circ}$ , is slightly soluble in formic acid and readily soluble in chloroform or benzene, and crystallises in minute plates melting at  $196-197^{\circ}$  (Found: C = 39.8; H = 2.2.  $C_8H_5O_2Cl_3$  requires C = 40.1; H = 2.1 per cent.).

When boiled for five minutes with formic acid, it is completely converted into terephthalic acid, which was identified by its insolubility and by conversion into the dimethyl ester melting at  $140^{\circ}$ . Methyl *o*-trichloro-*p*-toluate crystallises from dilute methyl alcoholic solution in long, attenuated plates and melts at  $55^{\circ}$ . It possesses a pleasant, fruity odour, no pungency being detectable at the ordinary temperature (Found: C = 42.1; H = 2.8.  $C_9H_7O_2Cl_3$  requires C = 42.6; H = 2.8 per cent.).

The ethyl ester consists of colourless plates which melt at  $57^{\circ}$  and also have a faint fruity odour. *o*-Trichloro-*p*-toluamide separates from benzene in colourless needles and melts at  $180^{\circ}$  (Found: N = 5.6.  $C_8H_5ONCl_3$  requires N = 5.9 per cent.).

#### *Preparation of the Phthalaldehydic Acids, $CHO \cdot C_6H_4 \cdot CO_2H$ .*

[With HERBERT CLAYTON.]

The difficulty which has been experienced hitherto in preparing the phthalaldehydic acids is referred to in the introduction (p. 2205) and it is there stated that the hydrolysis of the *o*-dichlorotoluoyl chlorides furnishes a ready means of obtaining these important acids in quantity. Several hydrolytic agents may be used to bring about the conversion of the *o*-dichlorotoluoyl chlorides into the corresponding phthalaldehydic acids, but the conditions must be so selected that oxidation of these readily oxidisable acids may be avoided. This difficulty may be overcome by boiling the dichlorotoluoyl chloride with milk of lime in an atmosphere of carbon dioxide for three hours, or more conveniently in the following manner: The *o*-dichlorotoluoyl chloride (22.4 grams) is mixed with hot water (300 c.c.) in a flask of at least 1500 c.c. capacity,

and excess of precipitated calcium carbonate (28 grams) carefully added. The aqueous suspension is boiled for three hours under a reflux condenser fitted with a Bunsen valve, and the solution mixed with an excess of hydrochloric acid and allowed to remain over-night out of contact with air. The acid is rapidly collected by the aid of the pump, and the filtrates in the case of the *o*- and *m*-acids are extracted with ether (this is particularly necessary in the case of *o*-phthalaldehydic acid, which is appreciably soluble in cold water), the whole is then dried in a vacuum desiccator. Obtained in this way, the phthalaldehydic acids are pure enough for most purposes, but they may be recrystallised from formic or acetic acid or preferably from chloroform. In the case of the *m*- and *p*-acids, which are only slightly soluble in chloroform in the cold, extraction with boiling chloroform (in which any phthalic acid present is practically insoluble) is to be recommended. The hydrolysis of the  $\omega$ -dichlorotoluoyl chlorides proceeds almost quantitatively in the direction of the formation of the phthalaldehydic acids, and the over-all yield of these acids from the corresponding toluic acid is about 70 per cent. of that theoretically possible.

*o*-Phthalaldehydic acid, obtained by the hydrolysis of  $\omega$ -dichloro-*o*-toluoyl chloride under the conditions given above, was recrystallised from chloroform. It then softened at 95° and melted at 100.5°, whereas the melting point recorded is 97° (Racine, *Annalen*, 1887, 239, 82).

*m*- or *iso*Phthalaldehydic acid, prepared from  $\omega$ -dichloro-*m*-toluoyl chloride, separated in minute needles melting, in accordance with the observation of Simonis (*Ber.*, 1912, 45, 1585), at 175°, whereas Reinglass (*Ber.*, 1891, 24, 2423) observed the melting point 164–166°. *p*- or Terephthalaldehydic acid, from  $\omega$ -dichloro-*p*-toluoyl chloride, after recrystallisation from chloroform, melts at 248–250° when the melting-point tube is filled with carbon dioxide. Our experience confirms the ready oxidisability of this acid at its melting point by air observed by Wegscheider and Suida (*Monatsh.*, 1912, 33, 1009).

One of us (W. D.) wishes to thank the Ramsay Memorial Fellowship Trust for a Fellowship which has greatly facilitated this research.

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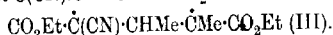
[Received, August 8th, 1922.]

CCLXV.—*Ethyl  $\alpha$ -Cyano- $\beta$ -methylglutaconate and its Methyl Homologues.*

By EDWARD HOPE.

IN connexion with work on the addition of hydrogen cyanide to the esters of cyanoglutaconic acids, described in the following paper, some observations on the behaviour of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate and two isomeric methyl homologues were made, which throw some light on the constitution of the latter two substances.

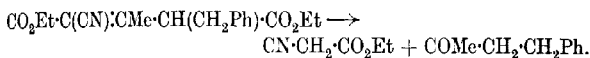
Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate was first made by Rogerson and Thorpe (T., 1905, **87**, 1669) by the condensation of ethyl acetoacetate with ethyl sodiocyanoacetate, and the constitution  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMc}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  was assigned to it. This ester forms alkali derivatives, which received formulæ such as  $\text{CO}_2\text{Et}\cdot\text{CK}(\text{CN})\cdot\text{CMc}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , and to the methyl derivative obtained from these by the action of methyl iodide was assigned the constitution  $\text{CO}_2\text{Et}\cdot\text{CMc}(\text{CN})\cdot\text{CMc}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  (I), this substance being isomeric with the compound obtained by the condensation of ethyl methylacetoacetate with ethyl sodiocyanoacetate, to which was given the constitution  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMc}\cdot\text{CMc}\cdot\text{CO}_2\text{Et}$  (II). At a later date (P., 1912, **28**, 51), Thorpe corrected his view of the constitution of the substance originally written as (I) and suggested the formula  $\text{CO}_2\text{Et}\cdot\text{C}(\text{CN})\cdot\text{CMc}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$  or



The present investigation provides experimental evidence for these corrected views. In the first place, a fresh means of differentiation between the esters (II) and (III) has been obtained by the action of concentrated aqueous ammonia in the cold. The ester (II) dissolves on shaking with aqueous ammonia in the course of a few minutes and deposits a mass of crystals which prove to be ethyl  $\beta$ -amino- $\alpha$ -methylcrotonate (IV),  $\text{NH}_2\cdot\text{CMc}\cdot\text{CMc}\cdot\text{CO}_2\text{Et}$ , melting at  $50-51^\circ$ , whilst there remains in the aqueous solution a product, which decomposes at about  $320^\circ$ , formed by the interaction of methylacetoacetic ester or the above amino-ester and cyanoacetamide. This substance is evidently identical with that obtained by Guareschi in his investigation of the reaction between methylacetoacetic ester and cyanoacetic ester in the presence of ammonia (*Mem. Accad. Sci. Torino*, 1896, **46**, 1). On boiling with alkalis, the substance of melting point  $320^\circ$  gives off ammonia and there remains the alkali salt of 6-hydroxy-2-keto-4 : 5-dimethyl-2 : 3-dihydropyridine-3-carboxylonitrile, which on acidification gives the free nitrile, melting at  $276^\circ$  (Guareschi gives  $270-272^\circ$ ).

On the other hand, the isomeric ester (III), when shaken with ammonia, dissolves only very slowly and even on repeated shaking for two or three hours is mainly unaffected. If allowed to remain in contact with the ammonia, however, for twelve to twenty-four hours and frequently shaken, the solution deposits crystals of ethyl  $\beta$ -amino- $\alpha$ -methylcrotonate, and the aqueous solution contains the same substance as in the case of the isomeric cyanoglutaconate.

The interpretation of these results appears to be that the second of these esters passes slowly into the first in the presence of ammonia and then undergoes the same reaction with this reagent. This reaction is essentially the reversal of the Rogerson-Thorpe condensation, by hydrolysis, followed by the action of ammonia on the products of hydrolysis, giving cyanoacetamide and  $\beta$ -amino- $\alpha$ -methylcrotonic ester. There is one recorded instance of a similar hydrolysis of a derivative of cyanoglutaconic ester, namely, the hydrolysis of benzylmethylcyanoglutaconic ester by alkali hydroxide (Thorpe, *loc. cit.*), in which cyanoacetic acid and benzylacetone are produced according to the equation



This representation assumes that hydrolysis occurs at the ethylenic linking, but there is no real evidence that this is correct. If this assumption were made in the case of the hydrolysis by ammonia of the condensation product of ethyl methylacetoacetate with ethyl sodiocyanoacetate, then one would be led to the conclusion that this compound had the constitution (III) whilst the product of methylation of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate would have the constitution (II). In view of the result of subjecting the cyanodimethylglutaconic esters to further methylation (thereby producing an  $\alpha\beta\gamma$ -trimethyl derivative), it seems most improbable that formula (III) can represent the ester which forms the definite sodium derivative which is the parent of the trimethyl derivative.

This view is confirmed by the examination of the behaviour of the methylation product of  $\alpha$ -cyano- $\beta$ -methylglutaconic ester towards sodium ethoxide. When this ester is treated in the cold with an equivalent of sodium ethoxide in alcoholic solution for a minute or less and then poured into dilute mineral acid and the product extracted, it is found that more than half of the ester has been converted into its isomeride (as indicated by its behaviour with ammonia) and simultaneously some ethyl carbonate and a liquid boiling at about the boiling point of ethyl cyanodimethylcrotonate are formed. All this tends to prove that the methylation product of  $\alpha$ -cyano- $\beta$ -methylglutaconic ester cannot form a sodium derivative

of its own, but can react with sodium ethoxide either by passing into the isomeric form or by losing a carbethoxy-group, whereas the cyano-ester (II) forms a definite sodium derivative, from which it can be recovered quantitatively. These considerations render it almost certain that this ester must have the constitution (III), whilst the isomeric form made from methylacetoacetic ester and sodiocyanoacetic ester must have the constitution (II).

The behaviour of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate towards ammonia is similar to that of the dimethyl derivative (II), that is, it dissolves and hydrolysis occurs, but the products in this case can be obtained from solution only by strong cooling (which causes the separation of ethyl  $\beta$ -aminocrotonate). By the subsequent evaporation of the mother-liquors, a substance of high melting point is obtained which, on boiling with caustic alkalis, gives a substance identical with that obtained by Guareschi (*loc. cit.*) and which is apparently 6-hydroxy-2-keto-4-methyl-2:3-dihydropyridine-3-carboxylonitrile,  $\text{MeC} \begin{smallmatrix} \text{CH}(\text{CN})\text{CO} \\ \text{CH}-\text{C}(\text{OH}) \end{smallmatrix} \text{N}$ .

Hydrolysis of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate and its two isomeric methyl homologues was also effected by heating with small amounts of water at 170–180°. In the case of the monomethylglutaconate, the products consisted of alcohol, acetone, and ethyl cyanoacetate. In the other cases, however, although there was no difficulty in identifying methyl ethyl ketone as one of the products, the fraction boiling at 190–210° was found to contain methylacetoacetic ester as well as cyanoacetic ester. The attempt to identify cyanoacetic ester by the action of ammonia, therefore, did not result in the formation of cyanoacetamide but in the formation of the condensation product of high melting point mentioned on p. 2221, which establishes the existence of these esters in the presence of each other.

#### EXPERIMENTAL.

*Ethyl  $\alpha$ -Cyano- $\beta$ -methylglutaconate.*—In the preparation of this substance, the details given by Rogerson and Thorpe (*loc. cit.*) were followed in essentials, but in the numerous preparations carried out, a number of observations were made which seem worth recording. In the first place, these authors state that a yield of 60 per cent. of the theoretical can be obtained when ethyl sodiocyanoacetate is condensed in alcoholic solution with ethyl acetoacetate. In spite of many attempts, the yields have never been raised above 40 per cent. in the present work, although the conditions have been varied a good deal. They have usually been between 33 and 40 per cent. The effect of the presence of water in the alcohol is most marked. For the highest yields, the driest possible alcohol must

be used. The use of 95 per cent. alcohol instead of absolute alcohol reduces the yield to about 20 per cent. The best yields were obtained when potassium was substituted for sodium. In this case, the only departure from the details given by Rogerson and Thorpe is in the formation of the potassium ethoxide. This is conveniently done in the presence of dry ether. The ether must then be distilled off before adding the ethyl cyanoacetate. When potassium was used, the maximum yield obtained was 48 per cent. of the theoretical.

In view of the big effect of water on the reaction, it seemed desirable to attempt to remove the water formed in the reaction, since the establishment of an equilibrium seemed likely. None of the ordinary dehydrating agents could be used in this connexion, but an experiment was tried in which the usual quantities of materials were heated with a considerable amount of benzene so that the benzene distilled off continuously during the reaction. The yield of product was smaller than in those cases where benzene was absent and amounted to only 20 per cent. of the theory.

The condensation was also tried in the entire absence of alcohol by heating, with vigorous stirring, the sodium compound of ethyl cyanoacetate made in dry benzene, with ethyl acetoacetate. In this case the yield was even smaller and was about 10 per cent.

*Ethyl  $\alpha$ -Cyano- $\beta$ -dimethylglutaconate (Ethyl  $\alpha$ -Cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -butene- $\alpha$ -dicarboxylate).*—In the case of the condensation of ethyl sodiocyanoacetate with ethyl methylacetoacetate, the yield (to which no reference is made in the paper of Rogerson and Thorpe) is very small, being about 15–17 per cent. of the theoretical when sodium is used. It is raised to about 23 per cent. by using potassium.

*Action of Concentrated Aqueous Ammonia on Ethyl  $\alpha$ -Cyano- $\beta$ -methylglutaconate (I).*

Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate is mixed with about five times its weight of the strongest aqueous ammonia. It dissolves with a brownish-yellow colour, which fades considerably on keeping. After about twenty-four hours, the clear solution is cooled and a crystalline solid separates, which is filtered off as rapidly as possible. The filtrate is now evaporated to dryness in a vacuum, when a brownish-white solid remains.

The crystalline solid melts when allowed to reach atmospheric temperature, and that it consists to a large extent of  $\beta$ -amino-crotonic ester is shown by extracting it with ether and keeping the ether extract, which is at first oily, for a day or so, when it will solidify to large, monoclinic crystals which melt at 20–21°. This

is the metastable form of ethyl  $\beta$ -aminocrotonate. It was identical with a specimen made from pure acetoacetic ester.

The substance left after the evaporation of the mother-liquors from the crystalline solid has not itself been closely investigated. Satisfactory analytical results have not been obtained on account of the difficulty of recrystallising it without decomposition. When it is boiled with sodium hydroxide solution, however, until ammonia (which comes off in large amount) ceases to be evolved, a clear solution of a sodium salt is left which, on acidification, gives a white, crystalline precipitate of a sparingly soluble substance. This acidic substance can be recrystallised from water or methyl alcohol and when purified in this way melts at about  $316-319^\circ$  after previous darkening at about  $300^\circ$  (Found: C = 55.8; H = 4.2; N = 18.6.  $C_7H_9O_2N_2$  requires C = 56.0; H = 4.0; N = 18.7 per cent.).

In view of the extraordinary stability of the substance towards boiling caustic alkalis as well as towards mineral acids, there was little doubt that the nitrogen, or at any rate a part of it, is in a ring structure, and it was soon realised that the compound was identical with the substance made by Guareschi (*loc. cit.*) by the action of ammonia on a mixture of ethyl cyanoacetate and ethyl acetoacetate, namely, 6-hydroxy-2-keto-4-methyl-2:3-dihydropyridine-3-carboxylonitrile.

*Action of Ammonia on Ethyl  $\alpha$ -Cyano- $\beta$ -dimethylglutaconate (II).*

When this ester is treated with ammonia under the conditions employed in the case of its lower homologue, it does not dissolve at once to a clear solution, but when the mixture is shaken vigorously from time to time for about ten to fifteen minutes signs of a crystalline precipitate make their appearance. On the next day, the oil having entirely disappeared, the crystalline precipitate is filtered off, and the filtrate cooled strongly, when more crystals separate. These together with the first lot are treated with ether; a portion dissolves readily in the cold, leaving the rest unchanged. The soluble portion, after evaporation of the dried ethereal solution, separates in large crystals from a concentrated solution in ether and melts at  $51-52^\circ$ , the substance evidently being ethyl  $\beta$ -amino- $\alpha$ -methylcrotonate. A specimen of this, made by the action of ammonia on ethyl methylacetoacetate, melted at  $52^\circ$  and at the same temperature when mixed with the above product.

The evaporation to dryness of the aqueous mother-liquors left a brown solid, to which was added the substance insoluble in ether mentioned above. This substance can be recrystallised from water, but tends to lose ammonia if the heating with water is

prolonged. It consists of small, hard crystals which decompose and melt at about  $320^{\circ}$ . The substance is very sparingly soluble in methyl alcohol. The solution in water gives a deep blue coloration with ferric chloride. It gives off ammonia when heated in a dry tube and also when its aqueous solution is boiled with sodium hydroxide or carbonate. After boiling with the former until no more ammonia is evolved and acidifying the alkaline liquid, a sparingly soluble white solid is thrown out. This substance, which can be recrystallised from water or methyl alcohol, melts, when pure, at  $276^{\circ}$ . Like the substance of melting point  $316\text{--}319^{\circ}$  obtained in a similar manner from  $\alpha$ -cyano- $\beta$ -methylglutaconic ester, this compound is extremely stable towards boiling alkalis and mineral acids. It gives a bluish-violet coloration with ferric chloride. It gives no trace of ammonia when heated in a dry tube (Found: C = 58.7; H = 5.1; N = 16.8.  $\text{C}_8\text{H}_8\text{O}_2\text{N}_2$  requires C = 58.5; H = 4.9; N = 17.1 per cent.). It is evidently identical with the substance made by Guareschi (*loc. cit.*) by the action of ammonia on a mixture of ethyl methylacetoacetate and ethyl cyanoacetate and stated by him to be 6-hydroxy-2-keto-4:5-dimethyl-2:3-dihydropyridine-3-carboxylonitrile.

*Action of Ammonia on Ethyl  $\gamma$ -Cyano- $\alpha\beta$ -dimethylglutaconate (Ethyl  $\alpha$ -Cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -butene- $\alpha\gamma$ -dicarboxylate).*

When this ester is treated with concentrated ammonia in the same way as the two preceding ones, even on vigorous shaking, no appreciable effect is produced in an hour. The cyano-ester settles out apparently unchanged. Only by frequent agitation during twelve to twenty-four hours is the completion of the reaction ensured, and crystals of ethyl  $\beta$ -amino- $\alpha$ -methylcrotonate are then suspended in the liquid as in the case of the isomeric cyano-ester. The evaporation of the mother-liquors reveals the presence of the pyridine derivative of melting point  $320^{\circ}$ , and this, on boiling with alkalis, gives rise to the substance of melting point  $276^{\circ}$ . The relative amounts of the two products are exactly the same as in the case of the isomeric cyanodimethylglutaconate and there can be no doubt that the explanation of their behaviour is that the above ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -butene- $\alpha\gamma$ -dicarboxylate first slowly undergoes isomeric change, with shift of the double bond, into ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^{\beta}$ -butene- $\alpha\gamma$ -dicarboxylate, which then reacts easily with the ammonia.

If equivalent amounts of ethyl acetoacetate and ethyl cyanoacetate are shaken together in the presence of concentrated aqueous ammonia, practically the same result is obtained as when ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate is so treated. The results obtained



when ethyl  $\alpha$ -cyano- $\beta$ -dimethylglutaconate is treated with ammonia are reproduced exactly by subjecting a mixture of equivalent amounts of ethyl methylacetoacetate and ethyl cyanoacetate to the same treatment. It is thus fairly certain that the first action of the ammonia is a hydrolytic one, resolving the cyanoglutaconates into a mixture of ethyl cyanoacetate and ethyl acetoacetate or a derivative of this.

*Transformation of Ethyl  $\alpha$ -Cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -butene- $\alpha$ - $\gamma$ -dicarboxylate into its Isomeric Modification.*

In effecting this isomeric change, sodium (1.5 grams) was dissolved in alcohol (40 c.c.) and, after cooling the solution to the ordinary temperature, the above cyano-ester (15.9 grams) was added. The solution was shaken for about half a minute, quickly poured into cold, dilute hydrochloric acid, the precipitated oil extracted with ether, the ethereal solution washed twice with water, and the solute isolated in the usual way. The smell of ethyl carbonate was noticeable in the product and, on heating, 1—1.5 grams of a distillate boiling between 125° and 135° were obtained. On now applying a vacuum, a small amount of a distillate collected at 130—150°/15 mm., which was without doubt ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^{\alpha}$ -butene- $\gamma$ -carboxylate or an isomeride. The main fraction, however, came over at 158—168°/15 mm. and was clearly the unchanged starting material or an isomeride. The action of ammonia made it quite clear that isomeric change had occurred, for the product dissolved readily on agitation with this reagent, behaving in the same way and giving the same products as ethyl  $\alpha$ -cyano- $\beta$ -dimethylglutaconate.

*The Action of Water at 180° on the Cyanoglutaconic Esters.*

*Ethyl  $\alpha$ -Cyano- $\beta$ -methylglutaconate.*—When this ester (15 grams) was heated in a sealed tube for eight to ten hours at 180° with water (3.6 grams, that is, 50 per cent. in excess of that theoretically required to give ethyl cyanoacetate and acetone), almost complete hydrolysis took place. By distillation of the product, two fractions were obtained, b. p. 60—82° and 200—214° respectively. In the first fraction acetone was detected in quantity by the formation of its *p*-nitrophenylhydrazone (m. p. 140°, alone or mixed with an authentic specimen). The higher fraction, when redistilled, boiled mainly at 205—210° and on agitation with ammonia gave a white, crystalline precipitate of cyanoacetamide melting at 116° (alone or mixed with pure cyanoacetamide).

*Ethyl  $\alpha$ -Cyano- $\beta$ -dimethylglutaconate.*—When this ester (15 grams) was heated with water (3.4 c.c.) under the conditions described

above, the glutaconate was almost completely changed. Two main fractions were again isolated from the product. The first boiled at 65–85° and on treatment with *p*-nitrophenylhydrazine gave a hydrazone which melted at 125° and corresponded in every way with that of methyl ethyl ketone. The less volatile fraction boiled between 195° and 210°, but on treatment with ammonia did not behave like ethyl cyanoacetate, not dissolving at once but requiring considerable agitation. After twenty to thirty minutes, a crystalline precipitate formed and this proved to be a difficultly fusible compound which gave a substance, m. p. 276°, when boiled with alkalis. This substance is clearly identical with that described on p. 2221, and is formed by the action of ammonia on a mixture of ethyl cyanoacetate and ethyl methylacetoacetate. Evidently, the hydrolysis is not so complete as in the case of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate.

*Ethyl  $\gamma$ -Cyano- $\alpha\beta$ -dimethylglutaconate.*—When this ester was subjected to the same treatment as the foregoing, exactly the same result was obtained. No difference whatever could be detected at any point.

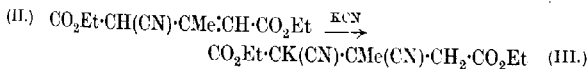
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CCLXVI.—*The Addition of Hydrogen Cyanide to Derivatives of Glutaconic Acid. Part I. The Addition of Hydrogen Cyanide to Ethyl  $\alpha$ -Cyano- $\beta$ -methylglutaconate and its Homologues.*

By EDWARD HOPE and WILFRID SHELDON.

In the course of an investigation carried out by one of us some years ago on the reaction occurring between ethyl citraconate and ethyl sodiomalonate (T., 1912, **101**, 892), it was found necessary to devise a means for the synthesis of  $\beta$ -methyltricarballic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (I). The method then adopted depended on the interaction of potassium cyanide with ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate in alcoholic solution according to the scheme :



Ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate, derived from the potassium compound (III), yielded  $\beta$ -methyltricarballic acid on hydrolysis. This method sufficed at the time, but it has been since found that

the addition of hydrogen cyanide occurs almost quantitatively and with remarkable ease when the conditions first described by Lapworth (T., 1903, 83, 995) are employed, that is, when the unsaturated ester, dissolved in alcohol or aqueous alcohol, is treated with hydrogen cyanide in the presence of potassium cyanide (the latter ensuring the presence of the essential agent, cyanide ions).

It is noteworthy that addition of hydrogen cyanide takes place also when the unsaturated ester is shaken with an aqueous solution of potassium cyanide in the entire absence of alcohol. When ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate is treated with a strong aqueous solution of potassium cyanide, it first dissolves, but the homogeneous solution soon separates into two layers, the lower one of which consists of a solution of the potassium derivative of the additive product (III). The possibility of using purely aqueous solutions was important in investigating whether an ester without replaceable hydrogen, for example, ethyl  $\alpha$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate,

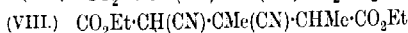
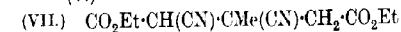
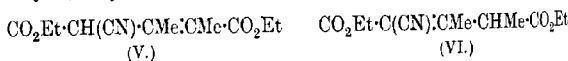


was capable of reacting with hydrogen cyanide or not.

The use of an aqueous alcoholic solution in a case like this results in the elimination of ethyl carbonate and the formation of ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate (compare Rogerson and Thorpe, T., 1905, 87, 1669).

The present communication contains an account of the chemistry of the products of interaction of hydrogen cyanide and ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate (II), ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^2$ -butene- $\alpha\gamma$ -dicarboxylate (V), and ethyl  $\alpha$ -cyano- $\beta$ -methyl- $\Delta^2$ -butene- $\alpha\gamma$ -dicarboxylate (VI). The reactions in the latter two cases are almost certainly identical since, under the conditions of the experiment, the cyano-ester (VI) passes over into (V). In any case, the products of reaction with hydrogen cyanide are identical.

In these reactions, the products are, respectively, from (II), ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate (VII), and from (V) and (VI) ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII).

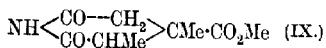


It is of interest to note that no addition of hydrogen cyanide could be detected in the case of ethyl  $\alpha$ -cyano- $\alpha\beta\gamma$ -trimethylglutaconate, which contains no hydrogen replaceable by metals. The general behaviour of the products VII and VIII is in accordance with the constitution given. For example, VII is hydrolysed by means of

concentrated hydrochloric acid or by 40 per cent. sulphuric acid to  $\beta$ -methyltricarballic acid, whilst VIII is hydrolysed by similar treatment to  $\alpha\beta$ -dimethyltricarballic acid\* (m. p. 165–167°).

The dicyano-esters also are much more acid in character than the cyanoglutaconates from which they are derived. The esters VII and VIII, for example, dissolve to some extent in a 10 per cent. solution of sodium carbonate and readily in potassium carbonate of equivalent strength, in both cases giving yellow solutions. Both esters, too, are readily attacked by a concentrated aqueous solution of ammonia. The cyanoglutaconates from which these esters are derived are practically not affected by alkali carbonates. They are, however, attacked by concentrated ammonia. The behaviour of the above dicyano-esters with ammonia is most remarkable, for it consists in nothing less than the complete reversal of the whole synthetical process from ethyl cyanoacetate and ethyl acetoacetate or a derivative. The product of interaction with ammonia, of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate (VII), for example, gives exactly the same products as arise in the similar treatment of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate, namely,  $\beta$ -aminocrotonic ester and the hydroxypyridine derivative described in the preceding paper (p. 2220). The same kind of reaction occurs with the dimethyl derivative (VIII),  $\beta$ -amino- $\alpha$ -methylcrotonic ester being produced along with the corresponding hydroxypyridine derivative.

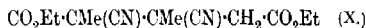
In view of the fact that ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate (VII) contains hydrogen replaceable by metals, a methyl homologue was prepared by the action of methyl iodide on the sodium derivative. A substance isomeric with the dimethyl derivative (VIII) was produced. The individuality of the new ester was established in several ways. When hydrolysed with 40 per cent. sulphuric acid, it yielded a substance which, on treatment with methyl-alcoholic hydrochloric acid, gave a new and highly crystalline solid containing nitrogen, which is probably an imide with the constitution (IX).



\* This is apparently the first preparation of this acid. The acid described by Michael (*Ber.*, 1900, **33**, 3757) as  $\beta$ -methylbutane- $\alpha\beta\gamma$ -tricarboxylic acid (that is,  $\alpha\beta$ -dimethyltricarballic acid), melting at 196–198°, was obtained by the hydrolysis of the methylation product of the substance which he formulated thus:  $(\text{CO}_2\text{Et})_2\text{CH} \cdot \text{CMe}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ . The substance obtained by condensing ethyl citraconate with ethyl sodiomalonate is not, however, as Michael thought, ethyl  $\beta$ -methylpropane- $\alpha\beta\gamma\gamma$ -tetracarboxylate, but ethyl butane- $\alpha\beta\gamma$ -tetracarboxylate,  $(\text{CO}_2\text{Et})_2\text{CH} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$  (Hope, T., 1912, **101**, 900), and Michael's acid is without doubt pentane- $\beta\gamma\delta$ -tricarboxylic acid,  $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , which does, in fact, melt at about 200°.

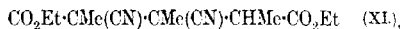
Under precisely the same conditions, ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII) yields the trimethyl ester of  $\alpha\beta$ -dimethyltricarballic acid.

The imido-ester is a white, crystalline solid melting at 135–136°. It dissolves in and can be titrated by *N*-potassium hydroxide solution. It suffers further hydrolysis when heated with concentrated hydrochloric acid in a sealed tube and gives  $\alpha\beta$ -dimethyltricarballic acid and ammonium chloride. The behaviour of the new ester (X) towards strong ammonia solution is also characteristic. It yields a sparingly soluble solid which gives no coloration with ferric chloride. This substance is probably an amide and not a pyridine derivative as in the other cases. The new dicyano-ester has without doubt the constitution



It would appear that in the case of these saturated substances, as in the case of the cyanoglutaconic esters, the hydrolytic action of ammonia depends on the presence of replacable hydrogen in the cyanoacetic ester residue.

By the action of sodium and methyl iodide, it was found possible to prepare the next homologue of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate, namely, the ester



which gives rise to  $\alpha\beta\gamma$ -trimethyltricarballic acid on hydrolysis.

Trimethyltricarballic acid appears to be incapable of separate existence, but its anhydride (m. p. 188–190°) and its trimethyl ester (b. p. 166–172°/26 mm.) were prepared.

#### EXPERIMENTAL.

##### *Addition of Hydrogen Cyanide to Ethyl $\alpha$ -Cyano- $\beta$ -methylglutaconate.*

##### *Formation of Ethyl $\alpha\beta$ -Dicyano- $\beta$ -methylglutarate (VII).*

This substance has been described in a previous communication (Hope, T., 1912, **101**, 911), but the method of preparation there employed gave neither a good yield nor a pure product. The following method gives excellent results. Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate (22.5 grams; 1 mol.), dissolved in alcohol (95 per cent.) (120 c.c.), is treated with a solution of potassium cyanide (13 grams; 2 mols.) in water (70 c.c.). The homogeneous solution is cooled in ice-water and further treated with a quantity of approximately 20 per cent. aqueous hydrochloric acid containing 5.4 grams (1.5 mols.) of the acid. The reaction mixture, after standing at the ordinary temperature for fifteen minutes, is poured into about 500 c.c. of dilute hydrochloric acid, the precipitated oil extracted

with ether, the ethereal solution washed with water several times and dried with calcium chloride. After evaporation of the ether, the residual oil is distilled under reduced pressure. In such an experiment, 21 grams of the pure product were obtained, boiling at  $200-205^{\circ}/20$  mm. (yield 83 per cent. of the theoretical) (Found: C = 57.1; H = 6.7. Calc., C = 57.2; H = 6.3 per cent.).

Ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate is a colourless or slightly yellow, rather viscid oil not appreciably soluble in water. It dissolves readily in a 10 per cent. aqueous solution of potassium or sodium hydroxide, being apparently hydrolysed, since it is not reprecipitated on acidification of the solution. It is somewhat soluble in a 10 per cent. solution of sodium carbonate, forming a faintly yellow solution, but it is quite readily soluble in a potassium carbonate solution of equivalent strength. The ester is reprecipitated from these solutions in alkali carbonates on acidification. In its easy solubility in solutions of sodium and potassium carbonates the behaviour of this ester is in marked contrast to that of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate, which is unchanged by these reagents—and indicates considerably greater acidity of one of the hydrogen atoms.

*Action of Ammonia.*—The ester is readily soluble in concentrated ammonia, giving at once a slightly opalescent solution. After keeping for twenty-four hours at the ordinary temperature, the solution was subjected to reduced pressure, and the cooling effect caused the crystallisation of a low-melting solid which proved to be  $\beta$ -aminocrotonic ester. The ester was purified and recognised as described under the account of the action of ammonia on ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate (this vol., p. 2219). There remained in the aqueous mother-liquors a high-melting solid which, exactly as did the corresponding glutaconate, gave, on boiling with alkali, a substance melting at  $316-318^{\circ}$ , which is identical with that obtained from the cyanoglutaconate and is evidently 6-hydroxy-2-keto-4-methyl-2 : 3-dihydropyridine-3-carboxylonitrile (Guareschi, *Mem. Accad. Sci. Torino*, 1896, 46, 1).

*Hydrolysis of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylglutarate by Mineral Acids.*

*Formation of  $\beta$ -Methyltricarballic Acid.*—The best agent for effecting this hydrolysis was found to be concentrated hydrochloric acid (sulphuric acid was used in the earlier experiments, but the ultimate solution of the acid is somewhat troublesome in this method). Usually 12 grams of the dicyano-ester were boiled with 100 c.c. of concentrated hydrochloric acid until all the oil had passed into solution, five to six hours being the time generally required. The clear liquid was then evaporated to dryness and the solid mass thus obtained, extracted for a long period with ether. On evapor-

ation of the latter, 6 grams of the acid remained and readily solidified. On recrystallisation from formic or hydrochloric acid, the product melted at  $164^{\circ}$ , and the melting point was unchanged by further crystallisation. The acid was, of course, identical with the  $\beta$ -methyl-tricarballic acid previously prepared by one of us (T., 1912, 101, 909), using more or less the same method.

It was found that the above hydrolysis could be very rapidly effected (in about an hour) by heating at about  $140^{\circ}$  with sulphuric acid of 70 per cent. strength.

In the preparation of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate from ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate, a number of alterations in the method of adding the hydrogen cyanide were tried—more particularly because it was necessary in some later experiments to avoid the presence of alcohol in performing this reaction.

It was found, in the first place, that no alcohol is really necessary, although it is convenient, provided that the cyanoglutaconate is sufficiently violently agitated with the hydrogen cyanide solution. A larger excess of potassium cyanide, 3, 4, and 5 molecular proportions to 1.5 of hydrochloric acid, did not alter the yield of the product in any way.

In the case of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate, vigorous agitation with a concentrated solution of potassium cyanide leads to the same result. In this experiment, vigorous shaking from time to time during ten minutes results in the formation of a deep yellow emulsion, from which nothing can be extracted by means of ether. After allowing the emulsion to settle, it is found that a layer of potassium cyanide solution forms the upper portion, the yellowish-brown lower layer being apparently an aqueous solution of the potassium derivative of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate. The free ester is obtained by acidifying and extracting with ether. From an experiment like this, 9 grams of ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate yielded 8 grams of the pure dicyano-ester of b. p.  $197\text{--}200^{\circ}/19$  mm.

*Condensation of the Cyanohydrin of Ethyl Acetoacetate with Ethyl Sodicyanoacetate. Formation of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylglutarate (VII).*

On account of the difficulty of obtaining ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate in good yield, it was decided to try the preparation of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate by the direct condensation of the cyanohydrin of ethyl acetoacetate with ethyl sodicyanoacetate—a method suggested by the interesting experiments of Thorpe and Higson (T., 1906, 89, 1455) on the synthesis of substituted succinic acids by the condensation, for example, of acetone cyano-

hydrin with ethyl sodiocyanoacetate. The condensation was carried out as follows. To a solution of sodium ethoxide (4.4 grams of sodium in 70 c.c. of absolute alcohol) 22.6 grams of ethyl cyanoacetate were added, and the solution was cooled and added, in small quantities at a time, with continual shaking, to a solution of 31.4 grams of the cyanohydrin of ethyl acetoacetate in 30 c.c. of absolute alcohol. The reaction took place without appreciable rise of temperature, and the slightly yellow solution was found on the next day to have set to a solid yellow mass, the solid being essentially the sodium derivative of ethyl dicyano- $\beta$ -methylglutarate. The mass was stirred with dilute hydrochloric acid, the precipitated oil extracted with ether, and the extract distilled under reduced pressure, when 20 grams of the expected condensation product were obtained, b. p. 197—202°/18 mm. The fact that the yield (40 per cent.) is the same as that obtained in proceeding through the stage of the cyanoglutaconate suggests that the mechanism of the formation of the dicyano-ester is essentially the same as that in the previously described experiments.

That the dicyano-ester prepared by this method is identical with that prepared by other methods was amply proved by a number of reactions. It gave  $\beta$ -methyltricarballic acid on hydrolysis. It was easily soluble in alkali hydroxides and in 10 per cent. potassium carbonate solution. When treated with ammonia, it gave the same results as other specimens.

*Addition of Hydrogen Cyanide to Ethyl  $\alpha$ -Cyano- $\beta$ -dimethylglutaconate (V). Formation of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII).*

The cyanodimethylglutaconic ester necessary for these experiments was prepared by Rogerson and Thorpe's method (*loc. cit.*) with the difference that potassium was substituted for the sodium used by them (this vol., p. 2219).

In adding hydrogen cyanide to ethyl  $\alpha$ -cyano- $\beta$ -dimethylglutaconate, 24 grams of the latter were dissolved in 150 c.c. of alcohol and the solution was cooled in ice. A concentrated solution of potassium cyanide (13 grams) was added and subsequently a quantity of a 20 per cent. solution of hydrochloric acid equivalent to 5.4 grams of the anhydrous acid. After standing for fifteen minutes, the product was isolated by pouring into water and extracting with ether, 20 grams of pure ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII), b. p. 200—206°/20 mm., being obtained. This is 75 per cent. of the theoretical (Found: C = 58.5; H = 7.2; N = 10.3.  $C_{13}H_{18}O_4N_2$  requires C = 58.6; H = 6.8; N = 10.5 per cent.).



*Ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate* resembles ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate very closely in its general properties. It is a colourless oil insoluble in 10 per cent. sodium carbonate solution, slightly soluble in 10 per cent. potassium carbonate solution and in 10 per cent. potassium or sodium hydroxide.

*Action of Ammonia.*—When ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (5 grams) was vigorously shaken with concentrated ammonia (60 c.c.), it gradually dissolved, solution being complete in about ten to fifteen minutes, the liquid taking on a yellow colour. After twenty-four hours, crystals had separated. A part of these proved to be soluble in ether and were identified as ethyl  $\beta$ -amino- $\alpha$ -methylcrotonate (this vol., p. 2221), whilst the other portion was soluble in hot water, from which it crystallised on cooling. This substance blackened considerably above  $300^\circ$  and melted at about  $320^\circ$ . By decomposing this compound with boiling caustic alkali, a substance, m. p.  $276^\circ$ , was produced and this showed itself in every way identical with the substance obtained by the action of ammonia on  $\alpha$ -cyano- $\beta\gamma$ -dimethylglutaconic ester (this vol., p. 2221). It is clearly the substance first described by Guareschi (*loc. cit.*) and stated by him to be 6-hydroxy-2-keto-4 : 5-dimethyl-2 : 3-dihydropyridine-3-carboxylonitrile.

*Hydrolysis of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII). Formation of  $\alpha\beta$ -Dimethyltricarballic Acid,*  
 $\text{HO}_2\text{C}\cdot\text{CHMe}\cdot\text{CMe}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}.$

—The cyano-ester was hydrolysed by boiling with concentrated hydrochloric acid for about twelve hours, the resulting solution being evaporated to dryness and the residual solid extracted several times with ether. After the evaporation of the ethereal solution, the gummy residue of acid was dissolved in methyl alcohol, saturated with dry hydrogen chloride, kept over-night, and treated again in the same way after evaporating off at reduced pressure water and excess of alcohol. The acid was thus almost quantitatively converted into the trimethyl ester. The ester was extracted in the usual way and was obtained as a colourless liquid, b. p.  $162^\circ/22$  mm. (Found : C = 53.3; H = 7.3.  $\text{C}_{11}\text{H}_{18}\text{O}_6$  requires C = 53.7; H = 7.3 per cent.).

The trimethyl ester was hydrolysed in the ordinary way with alcoholic potassium hydroxide solution, and the resulting acid extracted with several lots of ether. After evaporation of the ether, an acid remained which showed no signs of crystallisation. Even after repeated evaporation of an aqueous solution and ultimately leaving for many weeks not only in a vacuum over sulphuric acid, but also for a period exposed to the air, it still remained a

comparatively mobile liquid. This was doubtless a mixture of the two possible isomeric forms of inactive  $\alpha\beta$ -dimethyltricarballic acid. A crystalline acid was ultimately obtained by heating the syrupy acid at  $180^\circ$  for six hours in a sealed tube with 30 c.c. of hydrochloric acid (22 c.c. of the concentrated acid and 10 c.c. of water). On extracting the product with pure ether, an acid was obtained which solidified readily and melted (after remaining in contact with porous porcelain) at  $147$ – $151^\circ$ . Afterwards it was found that an acid of this melting point could readily be obtained by hydrolysing the trimethyl ester with concentrated hydrochloric acid and evaporating to dryness. The further purification of the acid proved to be a tedious piece of work, for apparently traces of an isomeric acid of lower melting point accompany it. It was crystallised five times from hydrochloric acid before a constant melting point was obtained. Ultimately the acid melted at  $165$ – $167^\circ$  (effervescing violently at this temperature, doubtless forming an anhydride). A mixture of this acid with  $\beta$ -methyltricarballic acid (m. p.  $164$ – $165^\circ$ ) melted at about  $152$ – $153^\circ$  (Found: C = 46.7; H = 6.1.  $C_8H_{12}O_6$  requires C = 47.0; H = 6.0 per cent.). Attempts were made to isolate the isomeric acid the presence of which was suspected, but it must have been present in small quantity, for from the mother-liquors of the above crystallisation nothing could be isolated except what was obviously principally the acid of melting point  $165$ – $167^\circ$ .

$\alpha\beta$ -Dimethyltricarballic acid shows in neutral solution precisely the same uncharacteristic behaviour towards various metallic salts as  $\beta$ -methyltricarballic acid (compare T., 1912, **101**, 910). It is insoluble in light petroleum, chloroform, or benzene, but readily soluble in water or acetic acid. It crystallises well from formic acid and from hydrochloric acid. On being heated above its melting point, it loses water easily, apparently forming an anhydride. This remained gummy and no solvent was found from which it could be crystallised. The acid was regenerated on crystallising the gum from hydrochloric acid.

*The Addition of Hydrogen Cyanide to Ethyl  $\alpha$ -Cyano- $\beta$ -methyl- $\Delta^4$ -butene- $\alpha\gamma$ -dicarboxylate (VI).*

In the preceding paper (p. 2222), it is shown that the above ester is converted by the action of sodium ethoxide in cold alcoholic solution into the isomeric ester, ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethylglutaconate. In the circumstances in which hydrogen cyanide is added on, that is, in the presence of potassium cyanide and the free alkali formed from it by hydrolysis, it is almost certain that isomeric change precedes the additive process. If such change did not

occur, it is clear that the same product is to be expected. In fact, the dicyano-ester obtained showed itself in its behaviour on hydrolysis, in its behaviour with ammonia, and in its behaviour on treatment with sodium and methyl iodide, to be identical with that derived from ethyl  $\alpha$ -cyano- $\beta$ - $\gamma$ -dimethylglutaconate.

*Methylation of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylglutarate. Formation of  $\beta\gamma$ -Dicyano- $\gamma$ -methylbutane- $\beta\delta$ -dicarboxylate (X).*

In the preparation of this substance, ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate (25 grams) was added to a solution of sodium (2.3 grams) in alcohol (50 c.c.), and the mixture, after the addition of methyl iodide (25 grams), heated on a boiling water-bath for two and a half hours. The product, which was isolated in the usual way, boiled at 196–197°/17mm. and was a colourless, viscous oil (Found: C = 58.9; H = 7.3.  $C_{13}H_{18}O_4N_2$  requires C = 58.6; H = 6.8 per cent.).

When the ester was boiled with sulphuric acid of about 60 per cent. strength for three and a half hours and the liquor saturated with ammonium sulphate, an oil separated which showed no signs of solidification. It was extracted with ether, the ethereal solution dried, and the residue after the distillation of the ether treated with methyl alcohol and dry hydrogen chloride. After standing over-night, the methyl alcohol and hydrochloric acid were evaporated in a partial vacuum, the flask being immersed in boiling water, and the residue again treated with methyl-alcoholic hydrogen chloride. This second treatment resulted in the separation of a white, crystalline solid. Water was added and the mixture extracted with ether. The ethereal solution was washed with dilute sodium carbonate solution, dried with calcium chloride, and the solvent distilled. The residue solidified readily and completely. On distillation at reduced pressure, it boiled without decomposition at 219–224°/19 mm. From 10 grams of the original ester a total of 4.5 grams of the new substance\* was obtained. The distillate crystallised to a hard solid, which was recrystallised from water. Two recrystallisations raised its melting point to 136–137° and this was unaltered by further crystallisation. The substance dissolved in dilute alkali hydroxides and also in concentrated sodium carbonate solution, being reprecipitated on the addition of acids. It contains nitrogen and is in all probability an imide—the imido-group explaining the solubility in alkalis. Formula (IX) explains the behaviour of the substance so far as it has been examined

\* A specimen of 10 grams of ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII), prepared from ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethylglutaconate and hydrogen cyanide, was subjected to *precisely* the same treatment as that described above. In this case exactly 4.5 grams of the trimethyl ester of  $\alpha\beta$ -dimethyltricarballic acid were obtained.

(Found: C = 53.7; H = 6.3; N = 7.3.  $C_9H_{13}O_4N$  requires C = 54.2; H = 6.5; N = 7.0 per cent.).

The imido-ester can be roughly titrated with aqueous alkali: 0.203 gram neutralised 0.03564 gram of sodium hydroxide, whereas 0.203 gram of a compound of the above formula, if it neutralised one gram-equivalent, would require 0.0408 gram.

Further evidence in favour of the view expressed above regarding the constitution, was obtained on hydrolysis with concentrated hydrochloric acid.

This operation required five hours, using a sealed tube, at a temperature of about  $175^\circ$ . The aqueous solution was evaporated to dryness on the steam-bath, and the solid residue extracted with pure ether. A residue of ammonium chloride was left and the substance which passed into solution was shown to be  $\alpha\beta$ -dimethyltricarballic acid, for after two crystallisations from hydrochloric acid it melted at  $162$ – $164^\circ$  (alone or mixed with an authentic specimen). (To obtain  $\alpha\beta$ -dimethyltricarballic acid of maximum melting point,  $165$ – $166^\circ$ , requires, as a rule, five or six crystallisations.)

On vigorously shaking the cyano-ester (X) with concentrated ammonia solution, it gradually passed into solution and after six or seven hours a sandy solid separated in small amount. This substance, which increased a little in quantity after the mixture had been kept for some days, was excessively sparingly soluble both in methyl alcohol and in water. It melted at about  $265^\circ$  and, unlike the substances obtained by the action of ammonia on the other cyano-esters, showed no colour reaction with ferric chloride. It is probably an amide, no hydrolysis of the carbon chain having occurred in this case.

*Hydrogen Cyanide and Ethyl  $\alpha$ -Cyano- $\alpha\beta\gamma$ -trimethylglutaconate.*

Some of the trimethylglutaconate was made in the manner described by Rogerson and Thorpe (T., 1905, **87**, 1669) by the action of sodium ethoxide and methyl iodide on ethyl  $\alpha$ -cyano- $\alpha\gamma$ -dimethylglutaconate in alcoholic solution. Owing to the formation of considerable amounts of ethyl  $\gamma$ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate by the action of traces of sodium ethoxide on the trimethylglutaconate, attempts were made to substitute metallic sodium and metallic potassium for the sodium ethoxide, alcohol being replaced by benzene.

Sodium was found scarcely to react, but with the aid of potassium, which formed an insoluble potassium derivative with the cyano-dimethylglutaconate, considerable quantities of the trimethylglutaconate, b. p.  $174$ – $178^\circ/28$  mm., were obtained. Unaltered

cyanodimethylglutaconate could be removed by the action of concentrated ammonia, the trimethyl derivative being unacted upon by this reagent.

In the investigation of the action of hydrogen cyanide on ethyl  $\alpha$ -cyano- $\alpha\beta$ -trimethylglutaconate, it was necessary to avoid the use of alcohol, since, owing to the presence of potassium cyanide, a certain amount of potassium ethoxide would have been formed, with the consequent elimination of ethyl carbonate and the formation of cyanotrimethylcrotonate. Agitation with an aqueous solution of potassium and hydrogen cyanides was the method adopted. The product in two separate experiments was identical with the starting material. It can therefore be safely concluded that ethyl  $\alpha$ -cyano- $\alpha\beta$ -trimethylglutaconate does not add on hydrogen cyanide.

*Methylation of Ethyl  $\alpha\beta$ -Dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate (VIII).*

*Formation of Ethyl  $\beta\gamma$ -Dicyano- $\gamma$ -methylpentane- $\beta\delta$ -dicarboxylate (XI).*

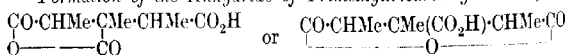
Since the above method for producing this substance failed, an attempt was next made to methylate ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylbutane- $\alpha\gamma$ -dicarboxylate and was found to be successful.

In methylating this substance, 18.9 grams of it were treated with sodium ethoxide, prepared by dissolving sodium (1.61 grams) in absolute alcohol (40 c.c.). Subsequently methyl iodide (20 grams) was added. The addition of the sodium ethoxide resulted in a bright red colour, and there was no evolution of heat. The mixture became hot, however, on the addition of methyl iodide. The reaction was allowed to proceed by itself for about one hour and the mixture was then heated gently for a similar period on the steam-bath. On pouring into water and extracting with ether in the usual way, 16 grams of a new substance, b. p. 202–207°/23 mm., were isolated (Found: C = 59.6; H = 6.8.  $C_{14}H_{20}O_4N_2$  requires C = 60.0; H = 7.0 per cent.).

This new substance, which is a colourless oil, is quite insoluble in 10 per cent. aqueous potassium hydroxide, and is hence readily distinguishable from the original cyano-ester. It dissolves with great difficulty on prolonged standing with concentrated ammonia, but the product has not been examined.

*Hydrolysis of Ethyl  $\beta\gamma$ -Dicyano- $\gamma$ -methylpentane- $\beta\delta$ -dicarboxylate.*

*Formation of the Anhydride of Trimethyltricarballic Acid,*



When the cyano-ester is boiled with 40 per cent. sulphuric acid, it is slowly hydrolysed, the original oil being replaced by the

hydrolysis product, which is itself insoluble and floats on the sulphuric acid. Some of the product solidified without further treatment and was filtered off and crystallised from formic acid, when, after two crystallisations, it melted at 188–190°. The bulk of the product, however, required extraction with ether. The extract was treated with methyl alcohol and dry hydrogen chloride, and the ester thus formed isolated in the usual way. Practically the whole quantity boiled at 166–172°/26 mm. Redistillation gave a good specimen of boiling point 164–167°/24 mm. (Found: C = 54.9; H = 7.3.  $C_{12}H_{20}O_8$  requires C = 55.4; H = 7.7 per cent.). There can be no doubt that this is the trimethyl ester of trimethyltricarballic acid.

*Hydrolysis of Methyl Trimethyltricarballylate.*—By means of alcoholic potassium hydroxide solution an acid was obtained which remained gummy and crystallised only on boiling its solution in hydrochloric acid to almost complete dryness. By a somewhat wasteful crystallisation from hydrochloric acid a substance, m. p. 187–189°, was obtained, identical with the compound, m. p. 188–190°, already referred to. A specimen crystallised from hydrochloric acid and dried in an exhausted desiccator over sulphuric acid was analysed (Found: C = 53.8; H = 5.9.  $C_9H_{12}O_5$  requires C = 54.0; H = 6.0 per cent.).

The substance is evidently the anhydride of trimethyltricarballic acid, for the acid itself requires C = 49.5; H = 6.4 per cent. This is further borne out by the titration of the above compound: 0.1554 gram required 20 c.c. of  $N/10$ -NaOH, whereas 0.1554 of an anhydro-acid,  $C_9H_{12}O_5$ , should require 23.3 c.c. The end-point, using phenolphthalein, was very difficult to find, and a pink colour of reasonable permanence was obtained only after long standing.

It was at once noticeable that the substance of melting point 188–190° did not effervesce on melting (or on heating even at 240°), whilst the other methyltricarballic acids evolve water with violence at their melting points.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed a portion of the cost of this investigation.

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# CCLXVII.—*Reduction of Thorium Oxide by Metallic Tungsten.*

By THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD.,  
LONDON (work conducted by COLIN JAMES SMITHELLS).

It is well known to workers on thermionic valves that the electron emission from tungsten is increased if the metal contains about 1 per cent. of thorium. This has generally been ascribed to the effect of metallic thorium (Langmuir, Brit. Pat. 148,132), although no explanation of the formation of the metal has been put forward. The following experiments show that thorium can be produced under certain conditions by reaction between tungsten and thorium.

A series of gas-filled lamps having tungsten filaments containing 0.7 per cent. of thorium were burned for various periods at different temperatures, and the filaments examined microscopically and chemically. If a thoriated filament is dissolved in a mixture of boiling hydrofluoric and nitric acids, the thorium will remain as a white residue (*Trans. Faraday Soc.*, 1921, **17**, 485), whilst any metallic thorium will dissolve. The filaments from the experimental lamps were examined in this way, and it was found that as the temperature and the time of burning were increased, the residue, on dissolving, became green, blue, or grey, and diminished in volume. After burning at a sufficiently high temperature, only a microscopic residue remained, and this consisted of grey, metallic crystals and contained no particles of thorium.

If, however, the filament is volatilised in a current of chlorine and air, a residue of thorium will be obtained, showing that a large part of the thorium is still in the filament.

TABLE I.

Temperature of filament. °K.*	Time in hours.	Residue after dissolving.	Remarks.
2580	24	White ThO <sub>2</sub> .	No reaction.
2600	"	Blue "	Some "
2630	"	Greenish-blue ThO <sub>2</sub> .	
2700	"	Slate grey "	
2750	"	No ThO <sub>2</sub> .	Reaction complete.
2800	"	"	" "
2650	12	White ThO <sub>2</sub> .	No reaction.
2650	600	Green "	Some "
2700	24	Slate grey ThO <sub>2</sub> .	" "
2700	100	No ThO <sub>2</sub> .	Reaction complete.

\* These temperatures are strictly comparable, but may differ from the absolute value by a small amount.

Table I shows the influence of time and temperature on the reduction of the thorium.

It is apparent from these experiments that when a filament containing thoria is burned at a temperature of about  $2700^{\circ}\text{K}$ ., the thoria is reduced by the tungsten, giving metallic thorium. From the colour of the thoria residues as the action proceeds, it appears that a secondary reaction also takes place. A microsection of a filament in which the reduction is complete shows the presence of a large number of bright orange-coloured inclusions. Fig. 1 is a photomicrograph of an unetched section of a filament after burning for three hundred hours at  $2850^{\circ}\text{K}$ . These inclusions are not metallic thorium, as thorium produced by reduction of

FIG. 1.



*Unetched section of tungsten filament containing 0.7 per cent. of  $\text{ThO}_2$  after burning for 300 hours at  $2850^{\circ}\text{K}$ .  $\times 400$ .*

thoria within a filament is not visible under the microscope, and moreover, they are not attacked by boiling hydrogen peroxide. To determine the nature of these inclusions, which appeared to be connected with the coloration of the thoria residues from dissolved filaments, a short spiral of tungsten wire was packed with ignited thoria, and the temperature gradually raised to  $3000^{\circ}\text{K}$ . by the passage of an electric current. The experiment has been carried out in pure dry argon, nitrogen, hydrogen, and in a vacuum, with the same result in each case. The surface of the thoria gradually becomes converted into a grey, metallic, crystalline mass, belonging apparently to the cubic system. It has not been possible to convert the whole of the thoria, and the unchanged part develops into large, prismatic crystals. The reaction proceeds very



slowly at 1500° K., but is completed in a few minutes above 2600° K.

The grey crystals are exceedingly stable towards acids and alkalis. After grinding the material, it was possible to remove most of the unchanged thoria by levigation in water, but the microscope showed that the residue was not homogeneous and consisted of a mixture of transparent crystals varying in colour from yellow to blue, in addition to the grey metallic crystals. This mixture, which is not attacked by hydrofluoric and nitric acids, was fused with sodium carbonate (Found: Th = 57; W = 26 per cent.). The grey material appears from its behaviour towards reagents to be a thorium-tungsten-bronze, and it is suggested that the coloured crystals are thoria containing a small proportion of the oxides of tungsten in solution. The colours of the thoria residues from dissolved filaments are probably due to the same cause. No bronzes of tungsten and the alkaline-earth metals have been described previously, although double bronzes with the alkali metals are known (Engels, *Z. anorg. Chem.*, 1903, **37**, 125).

From these experiments it appears that the main reaction taking place in the filament is the reduction of thoria to thorium by the tungsten. In addition, there is considerable evidence that the tungsten oxide formed combines with some unchanged thoria to form a thorium-tungsten-bronze.

If the composition of this substance is similar to that of the known bronzes, it will be of the form  $\text{Th}(\text{WO}_3)_n$ , where, by analogy,  $n$  may be from about 3 to 10, and it is clear that a large amount of metallic thorium may be produced for each molecule of bronze formed.

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### CCLXVIII.— $\gamma$ -Methylfructoside.

By ROBERT CHARLES MENZIES.

THE synthesis of  $\gamma$ -methylglucoside by Fischer (*Ber.*, 1914, **47**, 1980) and the investigation of its methylated derivatives (Irvine, Fife, and Hogg, *T.*, 1915, **107**, 524) would doubtless, in normal times, have been followed more quickly by the synthesis of the corresponding derivative of fructose, described in this paper.

The existence of a reactive unsubstituted methylfructoside was predicted by Irvine and Robertson (*T.*, 1916, **109**, 1311), but previous evidence has been circumstantial, although methylated derivatives of  $\gamma$ -fructose have been obtained from sucrose (*T.*, 1920, **117**, 207)

and from inulin (*ibid.*, p. 1486). No methylfructoside containing an unsubstituted  $\gamma$ -fructose residue has hitherto been prepared.

A dextrorotatory reactive methylfructoside has now been isolated from the products of the action of pure methyl alcohol containing hydrogen chloride upon fructose; it will be shown that the fructose residue in this compound is identical with that in sucrose and in inulin. The recent work on these two substances is well known. It is, however, convenient to summarise previous indications of the existence of  $\gamma$ -methylfructoside.

In 1895, Fischer (*Ber.*, **28**, 1160) heated a solution containing 10 per cent. of fructose and 0.5 per cent. of hydrogen chloride in dry methyl alcohol for forty-eight hours at 35°. By extraction of the resulting syrup with ethyl acetate he obtained a hygroscopic, amorphous mass, characterised by the ease with which it was hydrolysed with regeneration of fructose. Purdie and Paul (*T.*, 1907, **91**, 289) repeated Fischer's conditions as to concentration, but carried out the reaction at room temperature. Following the change polarimetrically, they found that the specific rotation of a solution containing approximately 10 per cent. of fructose changed from  $-56^\circ$ , the value four minutes after addition of the hydrogen chloride, to  $-4.65^\circ$  after four hours. A slow change in the reverse direction then commenced, the original value of  $-56^\circ$  being again reached after two hundred hours.

In their discussion of results, Purdie and Paul direct attention to the possible formation of a dextrorotatory methylfructoside and state that a dextrorotatory compound was actually isolated from a syrup which had deposited crystalline levorotatory tetramethyl fructose.

The work of Irvine and Robertson (*T.*, 1916, **109**, 1305) confirmed Purdie and Paul's general conclusions, but showed that the issue was complicated by the presence of acetone as an impurity in the methyl alcohol used. They also predicted the properties of the  $\gamma$ -fructose, of which the methylfructoside now described is the first synthetic derivative.

Using as solvent pure methyl alcohol free from acetone, and dried before use by repeated distillation over sodium, it has now been found that the optical rotations of solutions containing not more than 5 per cent. of fructose change sign in about twenty minutes from the time of addition of hydrogen chloride, and attain maximum positive values in little more than half an hour. On arresting the reaction at this stage by neutralisation of the acid, a feebly dextrorotatory syrup is obtained on removal of the solvent. This syrup gives analytical figures approximating to those required for a methylfructoside.

This change in the optical rotation is accompanied by condensation between the ketose and the alcohol, and in the case of a 2½ per cent. solution of fructose more than 85 per cent. of the sugar undergoes reaction in forty minutes at 20°. These figures show that the change is the most rapid of this kind hitherto encountered in the sugar group.

Treatment of the syrup with ethyl acetate leads to partial solution only, the insoluble portion displaying in methyl alcohol a specific rotation of  $-27^\circ$ . The fraction soluble in ethyl acetate is dextrorotatory,  $[\alpha]_D +25.3^\circ$  (in ethyl acetate),  $+26.6^\circ$  (in water), and consists essentially of  $\gamma$ -methylfructoside. It is, however, probable that ethyl acetate also dissolves small quantities of the levorotatory  $\alpha$ - and  $\beta$ -methylfructosides, as in one experiment five successive extractions with ethyl acetate gave products showing the following specific rotations:  $+35^\circ$ ,  $+29.8^\circ$ ,  $+31^\circ$ ,  $+16.9^\circ$ , and  $+9.3^\circ$ . The fourth and fifth extracts were of much lower concentrations than the others, so that the original syrup thus consisted of some unchanged fructose together with a mixture of methylfructosides, partly dextrorotatory and comparatively readily soluble in ethyl acetate, partly levorotatory and very sparingly soluble in ethyl acetate. The use of this solvent may consequently be expected to lead to a good, but not to a complete, separation between the dextrorotatory and levorotatory components of this mixture.

Analysis showed that the syrup remaining after removal of the ethyl acetate had the composition of a methylfructoside. The compound has, moreover, all the characteristics of the derivatives of a  $\gamma$ -sugar, being completely hydrolysed in the cold by 0.033 per cent. aqueous hydrogen chloride, the specific rotation meanwhile changing from  $+22^\circ$  to  $-64.3^\circ$  owing to the formation of fructose. Under similar conditions,  $\beta$ -methylfructoside is unattacked.  $\gamma$ -Methylfructoside decolorises  $N/500$ -potassium permanganate solution in thirty minutes, the same time, under similar conditions, being required by  $\gamma$ -methylglucoside, whilst  $\alpha$ -methylglucoside and  $\beta$ -methylfructoside required thirty hours.

The above data afford conclusive evidence that the dextrorotatory methylfructoside belongs to the  $\gamma$ -type, and the formation from fructose of a compound of this nature has now been definitely proved for the first time (see Irvine, Steele, and Shannon, this vol., p. 1069).

Identification of the ketose residue in  $\gamma$ -methylfructoside with that contained in sucrose and in inulin rests, as usual, on a comparison of the derived tetramethylfructoses. Tetramethyl  $\gamma$ -methylfructoside was first prepared from  $\gamma$ -methylfructoside by the silver oxide method. This was repeated three times, the product being then distilled and again methylated. From this, tetramethyl

$\gamma$ -glucose was prepared by hydrolysis, a solution containing approximately 1 per cent. of tetramethyl  $\gamma$ -methylfructoside and 0.25 per cent. of hydrogen chloride being heated at 100° for three hours.

The analytical and physical data of the above compounds are compared with those obtained for the corresponding compounds when prepared from sucrose and from inulin.

*Tetramethyl  $\gamma$ -methylfructoside.*

	C.	H.	OMe.
From inulin * .....	52.33	8.47	60.6
From fructose .....	52.30	8.91	60.7
$C_6H_7O(OMe)_2$ requires .....	52.76	8.86	62 per cent.

	$n_D$ .	B. p.	$[\alpha]_D$ .
From inulin * ...	1.4471	137—138.5°/12 mm.	+20.98° (in ethyl alcohol)
From fructose ...	1.4468	95—105°/0.15 mm.	+44.8° (in ethyl alcohol)

*Tetramethyl  $\gamma$ -fructose.*

	C.	H.	OMe.
From inulin * .....	50.88	8.57	53.2
From sucrose † .....	50.87	8.51	50.3
From fructose .....	50.44	8.54	52.55
$C_6H_7O_2(OMe)_4$ requires .....	50.85	8.47	52.5

	$n_D$ .	B. p.	$[\alpha]_D$ .
From inulin * .....	1.4554	148.5°/10 mm.	+32.9°
From sucrose † .....	1.4545	154°/13 mm.	+31.7°
From fructose .....	1.4545	95°/0.12 mm.	+24.64°

\* Irvine and Steele, T., 1920, **117**, 1487.

† Haworth, *ibid.*, p. 207.

The above figures indicate that the three sugars are essentially the same. The differences in the specific rotations in the case of the tetramethyl  $\gamma$ -methylfructosides are without doubt principally due to the different proportions of the stereoisomerides present in the two cases.

This factor does not interfere in the case of the tetramethyl  $\gamma$ -fructoses, but here, as already explained, the synthetic product is mixed with a little levorotatory tetramethyl fructose, derived from levorotatory methylfructoside dissolved by ethyl acetate.

In view of recent publications, it is prudent to state that it is intended in this laboratory to attempt the synthesis of sucrose from  $\gamma$ -methylfructoside.

# EXPERIMENTAL.

*Specification of Methyl Alcohol Used.*—It has been shown by Irvine and Robertson (*loc. cit.*) that their own results, as also those of Purdie and Paul, were profoundly modified by the presence of acetone in the methyl alcohol used as solvent, the ketone condensing

with the sugar to form methylfructoside-monoacetone. For the present work, methyl alcohol was used which was free from acetone, giving no precipitate of iodoform with a solution of iodine in *N*-sodium hydroxide solution. It was dried by repeated distillation over sodium, the fraction boiling between  $64.5^\circ$  and  $66^\circ$  being

FIG. 1.

- Curve I.  $2\frac{1}{2}\%$  Fructose at  $20^\circ$ .  
 Curve II.  $5\%$  Fructose at  $18^\circ$ .  
 Curve III.  $10\%$  Fructose at  $20^\circ$ .  
 Curve IV.  $10\%$  Fructose (Purdie and Paul).

Solvent, methyl alcohol free from acetone, dried by distillation over sodium some days before use.  $0.5\%$  Hydrogen chloride in each case.

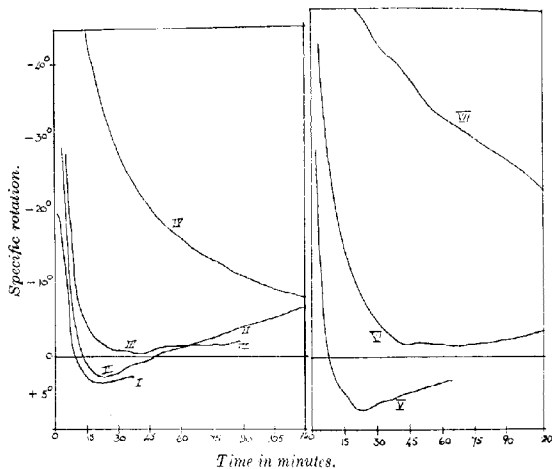
FIG. 2.

- Curve V.  $2\frac{1}{2}\%$  Fructose at  $20^\circ$ .  
 Curve VI.  $2\frac{1}{2}\%$  Fructose;  $1\%$  water at  $20^\circ$ .  
 Curve VII.  $2\frac{1}{2}\%$  Fructose;  $6.5\%$  water at  $20^\circ$ .

Solvent, methyl alcohol free from acetone, distilled over sodium immediately before use.  $0.5\%$  Hydrogen chloride in each case.

FIG. 1.

FIG. 2.



employed. The density corresponded with a methyl alcohol content of more than 99.5 per cent.

*Optical Data.*—Using the methyl alcohol specified above as solvent, solutions containing 0.5 per cent. of hydrogen chloride in each case and 10, 5, and 2.5 per cent. of fructose were prepared. The fructose was first dissolved in the pure solvent; dry methyl-

alcoholic hydrogen chloride was then added, the quantities being adjusted so that the desired solution was obtained on mixing.

Fig. 1 illustrates the changes with time of the specific rotations. For comparison, a curve is also shown displaying the changes in specific rotation calculated from Purdie and Paul's figures. Zero time in each case is that of addition of the hydrogen chloride.

It will be noted that the changes now under discussion were both greater in magnitude and more rapid than those observed by Purdie and Paul, and that in the cases of solutions containing 5 and 2.5 per cent. of fructose, the sign of the rotation quickly changed, a maximum positive value being observed in less than half an hour.

This result was directly contrary to that expected, since Irvine and Robertson (*loc. cit.*, p. 1310) wrote:

"The methyl alcohol which is recovered from the methylfructoside preparation, and is thus deprived of the last traces of acetone, condenses with fructose in a different manner. . . . No preliminary fall in *læv*orotation then takes place, so that the section A B in Purdie and Paul's curve is cut out" (Purdie and Paul, *loc. cit.*, p. 291).

This statement requires modification. Irvine and Robertson's solutions contained 10 per cent. of fructose; their methyl alcohol contained 5 per cent. of acetone. They showed that both acetone and alcohol condensed with fructose. These condensations and likewise the subsequent neutralisation of hydrogen chloride with silver carbonate involve the formation of water. Now it will be seen by reference to Fig. 2 that the addition of 1 per cent. of water to a solution containing 2.5 per cent. of fructose and 0.5 per cent. of dry hydrogen chloride in dry methyl alcohol is sufficient to inhibit the change in sign of the optical rotation otherwise observed. Larger quantities of water completely alter the shape of the curve.

These observations indicate that the changed optical behaviour described by Irvine and Robertson is to be attributed, not to the elimination of acetone, but to the introduction of water into their recovered alcohol.

This conclusion is strengthened by the following experiment.

The solution containing 5 per cent. of fructose (Fig. 1) was neutralised by careful addition of sodium dissolved in dry methyl alcohol. The solvent was then removed by slow distillation through a column. The first fraction was used for a similar experiment, the same concentration of fructose and of hydrogen chloride being used. The curve now obtained by plotting the rotations against the times was, within the limits of experimental error, identical with the first.

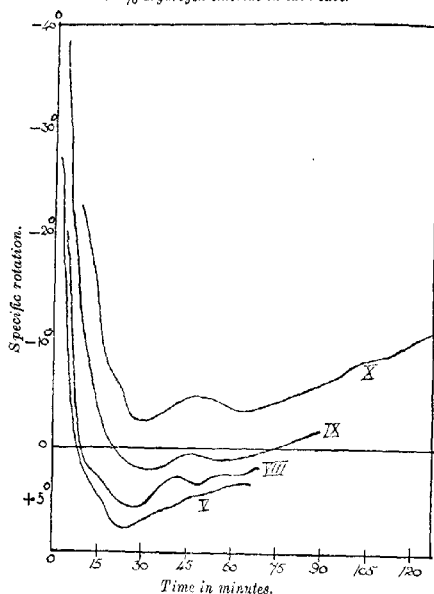
Further confirmation of the statement that the flattening of the

curve described by Irvine and Robertson was not due to the removal of acetone is afforded by the fact that acetone itself has an effect similar to that of water in altering the changes observed subsequent to the addition of hydrogen chloride (Fig. 3).

FIG. 3.

Curve V. 2½% Fructose at 20°.  
 Curve VIII. 2½% Fructose; 0·2% acetone at 20°.  
 Curve IX. 2½% Fructose; 1·4% acetone.  
 Curve X. 2½% Fructose; 5% acetone at 20°.

Solvent, methyl alcohol; distilled over sodium.  
 0·5% Hydrogen chloride in each case.



The above details are given partly at the direct request of one of the above authors, and partly because they indicate the great importance in this work of the purity of the methyl alcohol used.

#### $\gamma$ -Methylfructoside.

*General.*—The solutions containing 10 per cent. and 2·5 per cent. of fructose (Fig. 1) were neutralised after ninety and forty minutes, respectively. On removal of the solvent, the resulting syrups gave the following analytical figures—

	C.	H.	OMe.
Syrup from 10 per cent. fructose .....	41.9	7.4	16.2
Syrup from 2.5 per cent. fructose .....	42.8	7.5	15.9
$C_7H_{14}O_6$ (OMe) requires .....	43.3	7.2	15.9
$C_7H_{14}O_6$ requires .....	40	6.7	— per cent.

These figures indicate that the reaction is more complete in the more dilute solution, in which condensation of more than 85 per cent. of the fructose appears to have taken place. This syrup still reduced Fehling's solution.

*Details of Preparation of  $\gamma$ -Methylfructoside.*—Seven grams of fructose were dissolved in methyl alcohol. This solution was diluted with methyl-alcoholic hydrogen chloride so that the total volume amounted to 350 c.c., whilst the acid content was 0.5 per cent.

The rotation was observed at short intervals, the maximum positive value,  $[\alpha]_D + 6^\circ$ , being attained after thirty-two minutes. The acid was neutralised by careful addition of sodium methoxide solution until the reaction was neutral to litmus. The greater part of the solvent was removed by distillation on the water-bath at the ordinary pressure; the remainder in a vacuum desiccator. The resulting syrup was shaken with ethyl acetate previously dried over potassium carbonate. By this means sharp separation was effected, there being obtained a laevorotatory syrup insoluble in ethyl acetate ( $[\alpha]_D - 27^\circ$  in methyl alcohol).  $\gamma$ -Methylfructoside dissolved in the ethyl acetate, and on removal of this solvent was obtained as a colourless, hygroscopic syrup,  $[\alpha]_D + 25.2^\circ$  (in ethyl acetate),  $+ 26.6^\circ$  (in water).

Owing to its hygroscopic nature, drying for analysis was difficult, and had to be continued in a vacuum for more than twenty-four hours at  $90^\circ$  (Found: C = 43.6; H = 7.1; OMe = 14.8, 14.4.  $C_7H_{14}O_6$  requires C = 43.3; H = 7.2; OMe = 15.9 per cent.).

$\gamma$ -Methylfructoside, dissolved in water, gave no precipitate on immediate boiling with Fehling's solution; if, however, six hours were allowed to elapse before applying the test, perceptible reduction was observed. Standing for six hours at room temperature with N/100-hydrogen chloride led to marked evidence of hydrolysis, whilst boiling for one minute with N/10-acid was followed by a copious formation of cuprous oxide on subsequent heating with Fehling's solution.

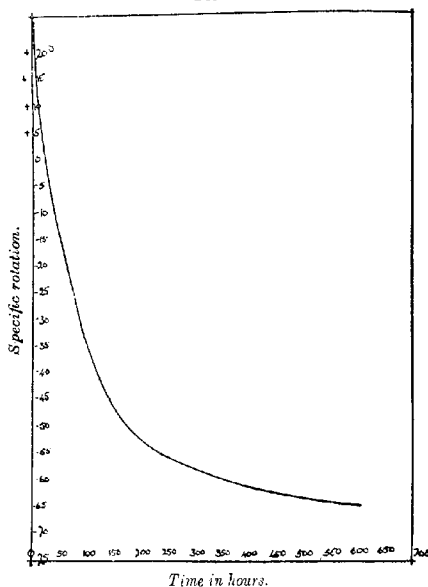
*Hydrolysis of  $\gamma$ -Methylfructoside.*—As the behaviour towards Fehling's solution indicated the compound to be unusually sensitive, an aqueous solution was made up containing 0.927 per cent. of  $\gamma$ -methylfructoside with 0.033 per cent. (= N/111) of hydrogen chloride. The temperature was never allowed to exceed  $20^\circ$ . The rotations were read in a 2-dcm. tube, the change of specific rotation with time being shown in Fig. 4. After an initial increase



from  $22.06^\circ$  to  $28.05^\circ$  (not shown) during the first thirty minutes, the specific rotation steadily decreased, changing sign after thirty hours, and reaching a value corresponding with a specific rotation of  $-64.26^\circ$  after twenty-seven days. It has recently been shown in this laboratory by Dr. J. Patterson that under much more drastic conditions the observed rotation of  $\beta$ -methylfructoside displayed no change.

The syrup obtained after neutralisation of the acid and removal of the solvent gave a phenylosazone, which had the same melting

FIG. 4.



point as glucosphenylosazone. The identity was further established by taking a mixed melting point.

*Tetramethyl  $\gamma$ -Methylfructoside and Tetramethyl  $\gamma$ -Fructose.*

All the operations involved in converting  $\gamma$ -methylfructoside into tetramethyl  $\gamma$ -methylfructoside and tetramethyl  $\gamma$ -fructose followed the lines usual in this laboratory, and do not require detailed description.

The analytical and physical data form an integral part of the main argument and have been consequently given in the introduction.

The author wishes to thank Principal Irvine for much help and advice throughout the progress of this work, and to express acknowledgment to the Carnegie Trust for a Fellowship, during the tenure of which the work was carried out.

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(CLXIX.—*Determination of the Molecular Weight of Substances in Alcoholic Solution from the Elevation of the Flash Point.*

By ROBERT WRIGHT.

THE flash-point apparatus here described was devised for the investigation of the selective solvent action of aqueous alcohol, an account of which is given in the following paper. The results obtained showed that the flash point of an alcoholic solution could be determined to within  $0.1^{\circ}$ , and it was thought that the method might be adapted to the determination of molecular weights of substances soluble in alcohol.

The flash point of a combustible liquid may be regarded as the temperature at which the air space over the confined liquid is rich enough in vapour to permit the passage of flame through the air-vapour mixture. It denotes a state of definite richness of vapour—or vapour pressure—for the given liquid and therefore is strictly comparable with the boiling point of a liquid, in that both represent temperatures of definite vapour pressure. It follows from this that the elevation of the flash point by means of a non-volatile solute should follow the same laws as the elevation of the boiling point.

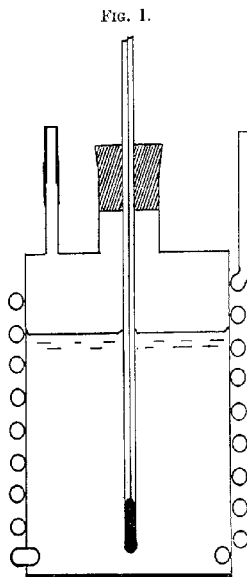
The flash-point constant—or the elevation of the flash point produced by the addition of a gram-molecule of solute to 100 grams of solvent—for alcohol will be given by the expression  $K = 0.027^{\circ} L$ . Its value will be less than that of the boiling point constant for the same liquid, as  $T$  will be lower and  $L$  greater in the case of the flash point. The flash point of pure alcohol in the apparatus used was found to be  $17.4^{\circ}$ . Young (*Proc. Roy. Dub. Soc.*, 1910, **12**, 441) gives 220.6 calories as the value of the latent heat of alcohol at  $20^{\circ}$ . Using this figure, we get 7.7 as the value of the flash-point constant, that of the boiling-point constant being 11.5. It will be evident that, from a knowledge of the flash point of pure alcohol and of that of an alcoholic solution of known composition, the

molecular weight of the solute may be found as in the boiling-point method.

As an alternative, the formula for the lowering of the vapour pressure,  $(p-p')/p' = n/N$ , may be used. The vapour pressure of pure alcohol at the temperature of its flash point is found from tables; this value is the same as the vapour pressure of the solution at the temperature of its flash point. The vapour pressure of the pure solvent,  $p$ , at the flash point of the solution is also found from tables. Then, since the vapour pressures of both solvent

and solution at the temperature of the flash point of the solution are known, and the composition of the solution is also known, we can calculate the molecular weight of the solute in the usual manner. All the flash points determined were between the temperatures  $17^{\circ}$  and  $19^{\circ}$ ; the vapour pressures of alcohol at these temperatures were taken as 36.8 mm. and 41.4 mm., and the vapour pressures at intermediate temperatures were found by assuming that the curve connecting the logarithm of the vapour pressure and the temperature is a straight line.

The standard form of flash-point apparatus as designed by Abel was at first employed, but it was not found possible to get results closer than about one degree, so a different type of apparatus was constructed in which the vessel is completely immersed in the heating bath, and the liquid is stirred by means of an air



current. The apparatus consists of a tinned copper cylinder 55 mm. in diameter and 75 mm. high. The top is fitted with two tubes, one carrying a thermometer graduated in tenths of a degree and the second—which is 20 mm. long and of 4 mm. bore—connected by means of rubber with a short piece of silica tube to act as a jet; this silica jet is essential, as without it the working of the instrument is very erratic. A second copper tube, which serves as an air heater, is wound several times round the cylinder in the form of a spiral; it then passes through the wall of the cylinder and is bent in the form of a ring lying close to the bottom of the vessel. The end of the spiral tube inside the vessel is closed and

the ring is pierced with a number of fine holes so that on passing air through the spiral the liquid in the cylinder is effectively stirred.

In carrying out a flash-point determination, a definite quantity (100 c.c.) of liquid is placed in the vessel, which is then placed in a beaker of about 2 litres capacity to act as a heating bath, the apparatus being completely immersed in the water up to the rubber connexion of the silica jet. The spiral tube is then connected through a calcium chloride drying-tube with a gas holder filled with air, a spring clip being placed on the rubber tube connecting the spiral and the drying-tube. The bath is heated by a very small flame and is stirred from time to time; the rate of heating being about one degree in fifteen minutes. At intervals of about two minutes the flame is removed, the bath stirred, and a series of short gusts of air admitted through the spiral by actuating the spring clip, until the temperature shown by the thermometer is quite constant. The small flame is then held close to the silica jet, and a further series of air gusts are passed through the liquid. The alcohol vapour carried by the air burns at the jet, and, if the flash point has been reached, the flame will strike back into the vessel with a slight explosion. If the temperature is below the flash point, the flame is replaced below the bath and the temperature allowed to rise a few tenths of a degree, when the flash test is repeated as before, the heating and testing being repeated every few minutes until the flash point is passed. After a flash has been obtained, the products of combustion are swept out of the vessel by a stream of air, the bath is cooled about  $1^{\circ}$ , and the process repeated with smaller temperature intervals between the tests. At least four flash points are obtained in this manner, and the lowest is taken as the true flash point. With due care, the flash point can be obtained with an accuracy of  $0.05^{\circ}$ . The following points are important: (1) The same volume of liquid should always be used in the apparatus. (2) The temperature of the vapour should be quite constant before a flash test is applied. (3) It should be made perfectly certain that the flash point has not been reached before the temperature is again raised, that is, about a dozen short air gusts should be passed while the flame is held to the jet. (4) The products of combustion should be swept out immediately after a flash. (5) Care should be taken not to wet the inside of the jet by stirring the liquid with too violent a stream of air. Should this occur, the jet may be dried by filter-paper wrapped round a glass rod.

The solutions used are prepared by weighing the solute in a graduated 100 c.c. flask, filling with alcohol to the mark, and again weighing. The contents of the flask are then poured into the apparatus and tested in the manner already described. After a

test has been completed, the apparatus is washed out and dried by heat and a current of air.

The results obtained for a number of solutes are shown in the table. Molecular weight *A* is calculated by taking the value 7.7 as the flash-point constant, whilst molecular weight *B* is calculated from the lowering of the vapour pressure.

	Grams of solute.	Grams of solvent.	Flash point elevation.	Molecular weights.		
				<i>A.</i>	<i>B.</i>	True.
Carbamide .....	2.45	76.36	0.40°	61.5	61.7	60
Acetanilide .....	5.62	75.21	0.45	127	127	135
Benzoic acid.....	7.63	74.54	0.60	130	126	122
Aniline .....	5.33	75.70	0.55	98	94	93
Benzyl alcohol .....	5.29	75.08	0.50	109	110	108

It will be seen that these results are accurate to within about 5 per cent., that is, they are comparable with those obtained by the boiling-point method. It should be pointed out, however, that the manipulation is somewhat tedious and that for accurate results somewhat high concentrations of solute must be used. On a flash-point elevation of about 0.50° and with a limit of 0.05° in the accuracy of its determination, the error in the molecular weight would be about 10 per cent.

The investigation was confined to ethyl alcohol, although other alcohols would probably be satisfactory. Benzene and other substances rich in carbon burn with a smoky flame which fouls the jet and renders accurate work impossible; moreover, the flash point of benzene is below its freezing point. It should be noted that the flash point obtained with the apparatus described is higher than that given by the standard Abel instrument, and that it will be greatly affected by the size of jet used.

A final point might be mentioned. The flash point of petroleum has long been known to be affected by atmospheric pressure. A fall of 10 mm. in the barometric height lowers the flash point by about 0.3° (Redwood, "Petroleum and its Products"). This lowering is usually accounted for by the greater ease of evaporation at the lower pressure. But if the flash point depends only on the vapour pressure of the liquid, it should not be affected by change of barometric pressure, although the time taken for the liquid to come into equilibrium with its vapour would be longer at high pressures. A series of flash points was taken at pressures from 750 mm. to 770 mm. and in all cases the value 17.4° was obtained for alcohol. The effect obtained in the case of petroleum may be due to the complex nature of the liquid.

*CCLXX.—Selective Solvent Action by the Constituents of Aqueous Alcohol.*

By ROBERT WRIGHT.

It is well known that when dealing with a mixed solvent, such as aqueous alcohol, many substances will dissolve in the mixture which are soluble in only one of the constituents. For example, sucrose is insoluble in pure alcohol but will dissolve readily in alcohol mixed with water; and on the other hand, many substances insoluble in water will dissolve in the water-alcohol mixture.

The question then arises: Are these solutes—or semi-solutes—really dissolved in both constituents of the mixed solvent, or are they simply held in solution by means of that constituent which has power to dissolve them when acting alone?

The question might be answered if we had a knowledge of the effect produced by a series of solutes on the partial vapour pressures of the water-alcohol mixture. Thus, sucrose, when added to water, will lower its vapour pressure, but will have no effect on alcohol, since it is insoluble in this solvent. When sucrose is dissolved in aqueous alcohol, will it lower both the partial vapour pressures or that of the water only? Again, benzyl alcohol is insoluble in water but soluble in ethyl alcohol. What effect will it have on the partial vapour pressures of the two constituents of the mixed solvent?

The most satisfactory method of investigating the partial pressures of the mixed solvent is by conducting a series of analyses of the vapour phase in equilibrium with the solvent when a series of different solutes are dissolved in it, and comparing the results with that given by an analysis of the vapour when no solute is present. This method is somewhat tedious, and the results obtained by it will be considered later.

As a preliminary method of investigation, the flash points of a series of aqueous alcoholic solutions were made use of; the apparatus and method of working being those already described for the determination of molecular weights (this vol., p. 2247). The flash point of the mixed solvent was first found, and then a series taken when different solutes were present. The results obtained are shown in Table I.

It is at once seen that the different solutes have very different effects on the flash point of the solution, and therefore at least on the vapour pressure of the alcoholic constituent. Benzyl alcohol, which is soluble in alcohol but not in water, raises the flash point of the solution, that is, lowers the partial vapour pressure of the

TABLE I.

Flash points of solutions of aqueous alcohol containing 44 per cent. of alcohol by weight.

Solute.	Grams of solute.	Grams of solvent.	Flash point.
None .....	—	—	30.5°
Sucrose .....	19.42	84.24	29.3
" .....	12.93	85.63	29.7
" .....	11.92	84.24	33.6
Benzyl alcohol .....	5.35	88.31	32.0
" .....	10.85	84.76	30.3
Glycerol .....	24.42	75.85	30.1
" .....			

alcoholic constituent. Sucrose, on the other hand, lowers the flash point and therefore presumably increases the vapour pressure of the alcohol; this may be due to the sucrose molecules hydrating themselves and thus rendering inert some water molecules and, as it were, leaving the solution richer in alcohol. Glycerol, which is miscible with both constituents, has also a slightly lowering effect on the flash point; it has therefore probably a greater attraction for the water than for the alcohol present in the mixture. It should be noted that the reasoning has ignored the effect of the solutes on the partial vapour pressure of the water component. It may be that sucrose, by lowering the aqueous vapour pressure and consequent removal of water vapour from the vapour phase, may lower the temperature of the flash point. Whether the sugar increases the vapour pressure of the alcohol or simply lowers that of the water can only be decided by the determination of the two partial pressures, and their comparison with those of the mixed solvent when no sucrose is present. In any case, it is quite clear that the various solutes are held in solution by different forces.

It was thought that some further information might be gained by the application of the freezing-point or boiling-point methods as used for molecular-weight determinations. The boiling-point method is not satisfactory, as it deals with the sum of the two partial pressures, and, unlike the flash point, does not differentiate between them. In the case of the freezing point, since the water alone freezes, it seemed possible that sucrose would still further lower it, whilst benzyl alcohol might have the opposite effect. Unfortunately, it was found quite impossible to obtain a definite freezing point for the water-alcohol mixture, the concentration of the alcohol being of necessity large; the separation of a relatively small amount of ice during freezing so altered the composition of the mixture by an unknown amount that no definite freezing point could be obtained. Several attempts were made to avoid this source of error, but were not successful, and the method had to be abandoned.

The analysis of the mixed vapours was carried out by passing a stream of air through the solution kept at a constant temperature in a thermostat and then leading the saturated air over heated copper oxide in a small combustion furnace, and estimating the carbon dioxide and water produced. The air was first purified by means of soda-lime and pumice moistened with concentrated sulphuric acid; it then passed through the heating coil of the flash-point apparatus already described (*loc. cit.*) and then through the solution, which was contained partly in the flash-point apparatus and partly in a set of absorption bulbs. The flash-point apparatus was fitted with a sensitive thermometer, and both it and the bulbs were placed in a thermostat at 20°. The saturated air next passed over the heated copper oxide and the carbon dioxide and water produced were collected in the usual manner. The exit tube of the absorption apparatus was connected with an aspirator fitted with a manometer.

In carrying out an estimation, the solution was brought to a temperature of 20° and the copper oxide heated. The aspirator was then set in action and the water collected in a 2-litre graduated flask. The volume of air aspirated was in all cases 2 litres, and the time occupied in the operation about three hours, the object of this slow rate of flow being to insure the complete saturation of the air with the mixed vapour. In cases where the room temperature fell a few degrees below that of the thermostat there was a tendency for the vapour to condense in the glass tube leading from the saturation bulbs to the furnace; this was corrected by warming the tube by means of a heated tile. When 2 litres of water had collected in the flask, the aspirator tap was closed and air forced through the purifying towers into the apparatus so as to restore atmospheric pressure, this being detected by the manometer. From the weight of carbon dioxide produced, the weight of alcohol vapour contained in the air was calculated. The corresponding weight of water was obtained by subtracting the weight of water produced by the combustion of the alcohol from the total water collected in the absorption apparatus. The barometric pressure and the room temperature at the time of the experiment were noted.

The partial pressures were calculated in the following manner. The weight of alcohol, calculated from the results of the combustion, divided by 46 gave the number of gram-molecules of alcohol. This value multiplied by 22,425 gave the number of c.c. of alcohol vapour in the air at *N.T.P.* This volume was designated  $V_{\text{алк}}$ . The corresponding value for water vapour,  $V_{\text{H}_2\text{O}}$ , was found in the same way. The air volume,  $V_{\text{air}}$ , was obtained by



reducing the volume aspirated (2 litres) to *N.T.P.* Then we have:

$$\frac{\text{Partial pressure of EtOH}}{\text{Barometric pressure}} = \frac{\text{Vol. of EtOH}}{\text{Total vol.}} = \frac{V_{\text{EtOH}}}{V_{\text{EtOH}} + V_{\text{H}_2\text{O}} + V_{\text{air}}}$$

The partial pressure of water was found by a similar calculation, and the results obtained are given in Table II.

TABLE II.

Partial vapour pressures for aqueous alcohol containing 38 per cent. of alcohol.

Solute.	Mole- cular conc.	Wt. of EtOH.	Wt. of H <sub>2</sub> O.	V. P. of EtOH.	V. P. of H <sub>2</sub> O.	Bar. press.	Temp.
None .....		0.105	0.0358	20.0	17.5	760	17°
" .....		"	0.0340	20.4	16.9	757	21
Sucrose .....	0.072	0.112	0.0296	21.4	14.5	764	17
" .....	"	"	0.0301	21.2	14.7	764	17
Benzyl alcohol ...	0.048	0.0975	0.0294	16.6	14.4	762	17
" " " " .....	"	"	0.0292	16.6	13.7	761	15
Glycerol .....	0.263	0.108	0.0335	20.9	16.4	760	18
" .....	"	0.112	0.0330	21.4	16.2	763	18

Molecular concentration gives the number of gram-molecules of solute per 100 grams of solvent. All vapour pressures were determined at 20°.

The values for water as obtained from the combustions are subject to error from the incomplete drying of the copper oxide and also from any error in the combustion of the alcohol vapour. In addition, the weights of water obtained are very small. A further series of determinations was carried out in which 4 litres of saturated air were aspirated over a tube filled with anhydrous copper sulphate and calcium oxide packed in alternate layers separated by glass wool. The alcohol vapour was not estimated. The results, which are in fair agreement with those given by the combustions, are recorded in Table III. The same aqueous alcohol was used in both series of experiments.

TABLE III.

Solute.	Mole- cular conc.	Wt. of water.	Bar. press.	Temp.
None .....		0.0693	749	16°
" .....		0.0712	756	18
Benzyl alcohol .....	0.133	0.0596	756	17
" " .....	"	0.0590	752	16
Sucrose .....	0.088	0.0602	747	16
" .....	"	0.0554	742	16

The results show fair agreement between the flash-point and combustion methods, in that the solutes, sucrose and glycerol, which

lower the flash point, raise the vapour pressure of the alcohol, whilst benzyl alcohol, which raises the flash point, lowers the alcohol vapour pressure. The partial pressure found for water in 38 per cent. aqueous alcohol is very close to that for pure water. This may possibly be due to errors inherent in the method, but such errors should apply equally to all the results, and are not of so much importance when considering the results relative to one another.

The effect of the different solutes may be considered in detail. The semi-solute, sucrose, lowers the vapour pressure of water and raises that of alcohol. The effect on water is quite normal, and that on alcohol may be explained by assuming that the sucrose molecules hydrate themselves and thus render some of the water inert and, as it were, leave the solution richer in alcohol. The second semi-solute, benzyl alcohol, lowers the vapour pressures of both alcohol and water, a somewhat unexpected result, as benzyl alcohol is insoluble in pure water. Such behaviour might be designated, although not explained, by the term "induced action." The amphi-solute, glycerol, which is soluble in both components of the solvent, is also abnormal, in that, instead of lowering both the partial pressures, it lowers only that of water, whilst it raises the alcoholic vapour pressure. As in the case of sucrose, this may be due to the hydration of the solute molecules, owing to the greater attraction between water and glycerol than between glycerol and alcohol.

#### *Summary.*

The term "semi-solute" has been used to designate a substance which is soluble in only one component of a mixed binary solvent, whilst "amphi-solute" has been used as the corresponding term for a substance soluble in both components.

The effect of the three solutes, sucrose, benzyl alcohol, and glycerol, on the partial vapour pressures of 38 per cent. aqueous alcohol has been investigated. The semi-solute, sucrose, raises the vapour pressure of the alcohol and lowers that of water; the semi-solute, benzyl alcohol, lowers the vapour pressure of each component of the solvent; whilst the amphi-solute, glycerol, behaves like sucrose in that it raises the vapour pressure of the alcohol and lowers that of water. Thus the result obtained in each case depends on the solute used and could not be predicted from the action of the solute on the separate pure components. It may be noted, however, that each of the semi-solutes lowers the vapour pressure of that constituent of the solvent in which it is soluble in the pure state; for example, sucrose lowers the vapour pressure of

the water, and benzyl alcohol lowers the vapour pressure of ethyl alcohol, although their effect on the second constituent of the solvent differs in the two cases.

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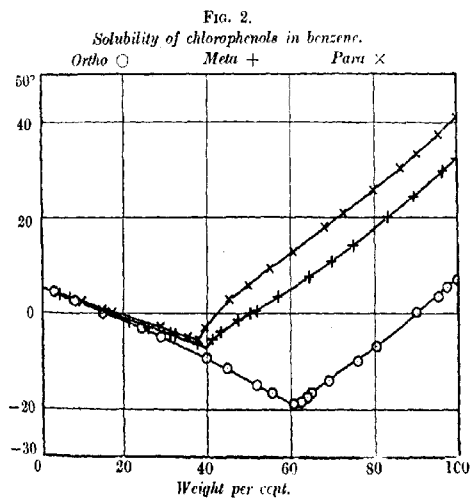
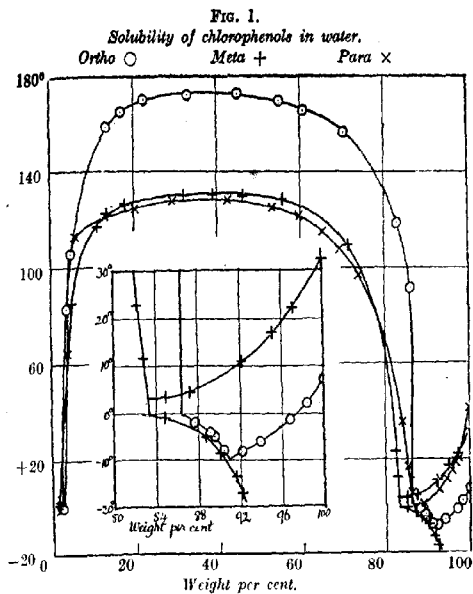
### CCLXXI.—*The Solubility of the Chlorophenols.*

By NEVIL VINCENT SIDGWICK and SYDNEY LEONARD TURNER.

THE isomeric chlorophenols differ in boiling point by more than 40°, and preliminary measurements (Sidgwick and Aldous, T., 1921, 119, 1011) showed that large differences occur also in their critical solution temperatures in water. It is therefore evident that, like the nitrophenols, they behave abnormally, the position of the substituents having a great effect on the vapour pressure and on the solubility. In the present paper their solubilities are examined in detail.

*Preparation of Materials.*—The ortho-compound was prepared by a method which was worked out in this laboratory by Mr. J. Back, and will shortly be published, by the chlorination of phenol with a solution of chlorine in carbon tetrachloride; it was purified as described by Wohlleben (*Ber.*, 1909, 42, 4369). The meta-compound was made from *m*-chloronitrobenzene by reduction and diazotisation, the latter process being carried out according to the directions of Mr. Back, to whom, and to Dr. E. Hope, we are much indebted for their kind assistance. The *p*-chlorophenol was made from *p*-chloroaniline. The benzene used had been freed from thiophen and purified by repeatedly freezing out. It melted at 5.3°.

*Measurement of Solubility.*—This was effected by the usual synthetic methods, either in glass bulbs (which were sealed for the higher temperatures) or, at lower temperatures, in a Beckmann apparatus. In many cases it was found convenient to use a "bracketing" method, with two adjustable thermostats, one above and the other below the solubility temperature, and to reduce the interval between them by successive steps to a fraction of a degree, the contents of the tube being always homogeneous in one and heterogeneous in the other. *m*-Chlorophenol in presence of water has a remarkable tendency to supersaturation. It was almost impossible without inoculation to cause the solid to crystallise from a mixture containing more than a few units per cent. of water; the solution remained homogeneous on cooling until it



reached the point at which ice separated. We were thus able to examine the ice curve unusually far into the metastable region, in fact up to 92 per cent. of phenol. If the solution was sown with a small crystal of the phenol, it solidified, and the corresponding point on the stable curve could be got by slow warming. The triple points were determined by a separate series of experiments.

The results are given in the following tables. The letters following the temperatures denote the phase in equilibrium with the solution (*i* = ice, *p* = solid chlorophenol, *B* = solid benzene, *L* = second liquid); metastable points are marked with an asterisk. The concentrations are expressed in grams of chlorophenol to 100 grams of solution. The values are plotted on Figs. 1 and 2; in Fig. 1, the region in which solid phenol separates is given as an inset on a larger scale (the curves for the para-compound being omitted to avoid confusion), in order to illustrate certain points which are discussed later.

TABLE I.  
Solubilities in Water.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
1.56	-0.20° <i>i</i>	0.73	-0.18° <i>i</i>	2.07	-0.2° <i>i</i>
2.44	-0.30° <i>i</i>	1.25	+1.2° <i>p</i>	3.91	+65.0° <i>L</i>
3.76	+82.9° <i>L</i>	1.85	2.5° <i>p</i>	10.66	113.8° <i>L</i>
5.12	106.3° <i>L</i>	5.12	85.25° <i>L</i>	20.50	125.0° <i>L</i>
13.58	159.1° <i>L</i>	11.13	118.0° <i>L</i>	29.16	128.2° <i>L</i>
16.95	165.8° <i>L</i>	13.56	123.0° <i>L</i>	42.57	128.7° <i>L</i>
22.59	170.7° <i>L</i>	17.84	127.5° <i>L</i>	53.49	125.8° <i>L</i>
33.00	173.0° <i>L</i>	32.02	130.8° <i>L</i>	59.62	122.4° <i>L</i>
45.04	172.9° <i>L</i>	38.89	130.7° <i>L</i>	65.05	115.5° <i>L</i>
54.95	170.1° <i>L</i>	46.12	130.5° <i>L</i>	69.36	107.7° <i>L</i>
60.72	166.20° <i>L</i>	55.65	129.1° <i>L</i>	74.03	97.0° <i>L</i>
70.62	156.6° <i>L</i>	71.23	109.8° <i>L</i>	84.02	35.3° <i>L</i>
82.82	118.9° <i>L</i>	82.30	23.1° <i>E</i>	85.42	17.0° <i>L</i>
85.90	91.5° <i>L</i>	82.90	11.8° <i>L</i>	86.19	5.5° <i>L</i>
87.73	-2.0° <i>i</i>	84.87	3.2° <i>p</i>	88.92	0.5° <i>p</i>
89.25	-4.0° <i>i</i>	"	-0.9° <i>i</i>	92.48	6.2° <i>p</i>
89.62	-5.0° <i>i</i>	87.19	+4.5° <i>p</i>	94.48	11.0° <i>p</i>
90.87	-8.0° <i>i</i>	88.66	-4.8° <i>i</i>	95.70	14.2° <i>p</i>
92.20	-8.2° <i>p</i>	90.11	-8.2° <i>i</i>	96.82	18.0° <i>p</i>
93.93	-6.0° <i>p</i>	91.73	-13.2° <i>i</i>	97.29	19.5° <i>p</i>
96.79	-1.5° <i>p</i>	92.23	+10.8° <i>p</i>	100	41.0° <i>p</i>
98.39	+2.0° <i>p</i>	"	-17.0° <i>i</i>		
100	+7.0° <i>p</i>	95.10	+17.0° <i>p</i>		
		97.11	+22.2° <i>p</i>		
		100	+32.5° <i>p</i>		
Critical solution temp.	173°		130.8°		129.0°
Triple points :					
ice- <i>L</i> <sub>1</sub> - <i>L</i> <sub>2</sub>	86.5°	83.4°	-0.4°*	—	—
ice- <i>p</i> - <i>L</i>	91.2°	—	—	—	—
<i>p</i> - <i>L</i> <sub>1</sub> - <i>L</i> <sub>2</sub>	—	82.3°	+3.2°	86.5°	-0.3°

\* Metastable point.

TABLE II.  
Solubilities in Benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
0.0	+5.3° <i>B</i>	0.0	5.3° <i>B</i>	0.0	5.4° <i>B</i>
3.04	4.6 <i>B</i>	4.31	4.0 <i>B</i>	2.98	4.5 <i>B</i>
8.33	2.7 <i>B</i>	7.00	3.2 <i>B</i>	10.25	2.4 <i>B</i>
15.49	0.0 <i>B</i>	15.32	0.5 <i>B</i>	15.10	1.0 <i>B</i>
24.56	-3.2 <i>B</i>	21.40	-1.4 <i>B</i>	17.62	0.2 <i>B</i>
29.01	-5.0 <i>B</i>	26.29	-2.9 <i>B</i>	29.14	-3.2 <i>B</i>
45.22	-11.6 <i>B</i>	31.77	-4.5 <i>B</i>	35.50	-5.0 <i>B</i>
55.54	-16.5 <i>B</i>	36.82	-6.0 <i>B</i>	38.07	-5.4 <i>p</i>
60.68	-18.8 <i>B</i>	38.39	-6.5 <i>B</i>	39.67	-3.2 <i>p</i>
62.50	-18.5 <i>p</i>	40.92	-7.2 <i>B</i>	45.65	-1.2 <i>p</i>
63.83	-17.4 <i>p</i>	41.66	-7.5° <i>B</i>	50.10	6.0 <i>p</i>
64.80	-16.4 <i>p</i>		-5.3 <i>p</i>	55.24	9.6 <i>p</i>
69.05	-13.7 <i>p</i>	43.62	-4.0 <i>p</i>	60.54	12.9 <i>p</i>
80.32	-7.0 <i>p</i>	44.90	-8.4° <i>B</i>	68.58	18.0 <i>p</i>
84.72	-3.8 <i>p</i>	47.78	-1.5 <i>p</i>	73.13	20.8 <i>p</i>
90.26	+0.2 <i>p</i>	50.68	0.0 <i>p</i>	80.06	25.8 <i>p</i>
95.20	3.6 <i>p</i>	51.81	+0.6 <i>p</i>	86.65	30.5 <i>p</i>
97.65	5.6 <i>p</i>	57.02	3.4 <i>p</i>	90.63	33.6 <i>p</i>
100	7.0 <i>p</i>	64.65	7.4 <i>p</i>	95.52	37.5 <i>p</i>
		70.00	10.7 <i>p</i>	100	41.0 <i>p</i>
		75.10	14.2 <i>p</i>		
		83.68	20.0 <i>p</i>		
		89.89	24.6 <i>p</i>		
		96.50	29.8 <i>p</i>		
		100	32.5 <i>p</i>		
Triple point :					
61.5	-19.5°	40.0	-7.0°	37.5	-5.5°

\* Metastable point.

*Nominal Heats of Solution in Benzene.*—These were calculated by means of the usual formula

$$Q = R \log_e \frac{s}{s_1} \times \frac{TT_1}{T_1 - T}.$$

Owing to the low melting points of the compounds, the solubility curves of the chlorophenols do not extend very far across the diagram, and so their heats of solution can be found only for a limited range. On the other hand, the solid benzene curves are long enough to make it worth while calculating the heats of solution of the benzene. It has already been pointed out (Sidgwick and Aldous, T., 1921, **119**, 1012) that the shape of the partial-pressure curves (and hence of the heat of solution curves) of both components of the system may be expected to be influenced in the same way by their degree of mutual solubility in the liquid state; where this is large the heat of solution will remain approximately constant, and where it is small the heat will show a large increase. The values obtained for the chlorophenols in benzene (which are given in Table III and plotted on Fig. 3) bear out this view. The changes

are smaller for the phenol than for the benzene; but in both cases the meta- and para-compounds show a distinctly greater increase than the ortho.

FIG. 3.

Heats of solution of chlorophenols in benzene and of benzene in chlorophenols.

Full curves . . . Chlorophenols. Dotted curves . . . Benzene.

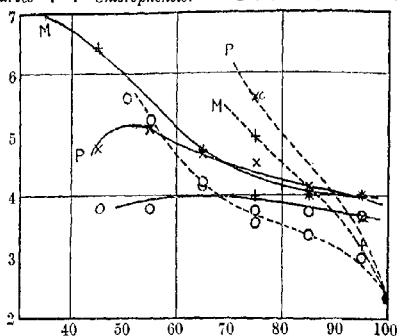


TABLE III.

Nominal Heats of Solution in Kgr.-Cals.

Mean mols. per cent.	Heat of solution of chlorophenol.			Heat of solution of benzene.		
	Ortho.	Meta.	Para.	Ortho.	Meta.	Para.
100	—	—	—	2.37	2.37	2.37
95	3.66	4.00	4.00	3.00	3.22	3.62
85	3.71	4.01	4.00	3.35	4.00	4.13
75	3.53	4.00	4.53	3.73	4.99	5.60
65	4.24	4.76	4.70	4.16	—	—
55	3.80	5.11	5.33	5.25	—	—
45	—	6.44	4.80	—	—	—
35	—	6.98	—	—	—	—

*Discussion of Results.*—The influence of position on the properties of the isomeric chlorophenols is of considerable interest. The phenols in general show the widest range of variation with position. The nitrophenols (T., 1915, **107**, 1202: 1921, **119**, 1001) and the hydroxybenzoic acids (T., 1921, **119**, 979) exhibit greater differences among the isomerides than have been observed elsewhere; the hydroxy-aldehydes, according to experiments performed in this laboratory but not yet published, appear to be equally abnormal. On the other hand, the effect of chlorine in promoting abnormality has hitherto been found to be extremely small. The chlorobenzoic acids (T., 1921, **119**, 998) are only very slightly abnormal, and so are the chloroanilines and the chloroacetanilides

(*ibid.*, p. 1013). We thus have in the chlorophenols a comparatively inefficient substituent in a very sensitive substance. The behaviour of the compounds shows that they are distinctly abnormal, both in vapour pressure and in solubility. Their boiling points differ by no less than 44°. Similar differences are found in the bromophenols and in the chlorocresols, as is shown in the following table, in which the chlorocresols are classified according to the relative positions of the chlorine and the hydroxyl.

	Boiling points.			Max diff.
	Ortho.	Meta.	Para.	
Chlorophenol .....	173°	214°	217°	44°
Bromophenol .....	195	237	238	43
Chlorocresol .....			223	42
(OH:Cl:CH <sub>3</sub> ) .....			238	
1:4:2.....				
1:3:2.....		225		
1:3:4.....		228		
1:2:4.....	196			

The differences in the critical solution temperatures in water are considerable and of the usual kind, that of the ortho being by far the highest, whilst those of the meta and para come close together; they may be compared with those of the nitrophenols and the hydroxytoluic (and hydroxybenzoic) acids, where, however, the differences are larger:—

	Ortho.	Meta.	Para.	Max. diff.
Chlorophenols .....	173.6°	130.8°	129.6°	44°
Nitrophenols .....	>200	98.7	92.8	>100
Hydroxytoluic acids .....	147	ca. 10	ca. 10	130
	(Mean)			

In the heats of solution in benzene, the differences, although they are of the usual kind, are much smaller than we should expect. For the *m*- and *p*-chlorophenols the values rise between 95 and 55 mols. per cent. only by 1.1 and 1.3 kgr.-cal., whilst for the nitrophenols the increases are 6.8 and 9.0, and for the hydroxybenzoic acids 14.2 and 12.5 kgr.-cal. between the same limits.

It is to be noticed that the abnormality of this group is more marked in those properties which are measured at high temperatures (boiling points, critical solution temperatures in water) than in those measured at low (solubility in benzene). This is an argument against the view that these abnormalities are due to association of the meta- and para-compounds, since association must diminish with rise of temperature. Hewitt and Winnill (*T.*, 1907, **91**, 441) found from surface tension measurements that the association factors of the chlorophenols in the neighbourhood of 100° were scarcely greater than unity (ortho 1.0, meta 1.11, para 1.07), and far smaller than those of the cresols (ortho 1.06, meta 1.33, para 1.26), the behaviour of which is normal.



The form of the solubility curves in water in the neighbourhood of the region where solid phenol separates (Fig. 1, inset) has several points of interest. In the first place, the ortho-compound has its eutectic point (ice, solid phenol, solution) on the chlorophenol side of the two-liquid area. In most if not all of the systems previously examined, where water forms two liquid layers with an organic substance, the eutectic point lies on the water side. The difference in this case is no doubt mainly accidental, and is due to the low melting point of the substance; but it is worth pointing out. The meta-compound has its eutectic as usual on the water side, at about  $-0.2^{\circ}$  and 0.8 per cent. The stable triple point (two liquids and solid phenol) is at  $+3.2^{\circ}$ . But owing to the strong tendency of this phenol to supersaturation it is easy to travel into the metastable area along the ice curve until it meets the two-liquid area at a metastable triple point (two liquids and ice) at  $-0.4^{\circ}$ . These two triple points appear on the phenol side of the two-liquid area at about 83.5 per cent. of phenol, and from the higher, the stable curve solution-solid phenol proceeds upwards to the melting point of the latter at  $32.5^{\circ}$ , whilst the metastable curve goes downwards from the metastable triple point at  $-0.4^{\circ}$ . The solubility curve of a solid always corresponds in form with its isothermal partial pressure curve, which becomes flattened in the neighbourhood of the point of separation into two liquids. Thus of the two *m*-chlorophenol curves in this figure the upper (solid phenol) corresponds with the form of the vapour-pressure curve of the phenol, and the lower (metastable, ice) to that of water vapour. It will be observed that all the solid curves in this region, whether rising or falling, are distorted from the normal form in the same way, becoming more horizontal as they approach the two-liquid area.

The two ice curves, that for *o*- (stable) and that for *m*-chlorophenol (unstable) run nearly parallel and quite close to one another. This enables us to calculate with unusual exactness the pressure of water vapour from equivalent solutions of high concentration of the two isomerides. At 87.0 per cent. by weight (48.4 mols. per cent. of phenol) the freezing points are: ortho  $-0.9^{\circ}$ , meta  $-2.4^{\circ}$ . At 91.0 per cent. (58.6 mols. per cent.) they are: ortho  $-8.3^{\circ}$ , meta  $-10.6^{\circ}$ . The vapour pressures of water and ice at these temperatures are known (Nernst, *Abh. Deutsch. phys. Ges.*, 1910, 12, 565), and so we can find the relative lowering of the vapour pressure of water by these quantities of the two isomerides. The percentage diminution of vapour pressure is

at 48.4 mols. per cent.: ortho 0.86, meta 2.33.

at 58.6 mols. per cent.: ortho 7.8, meta 9.8.

The corresponding effects in benzene can be calculated from the benzene curves, although only at a lower concentration. The freezing point of benzene is depressed by the presence of 45.0 grams per cent. (10.28 mols. per cent.) of the ortho-compound to  $-11.5^{\circ}$ , of the meta to  $-8.5^{\circ}$ , and of the para (by a slight extrapolation) to  $-7.6^{\circ}$ . Taking the molecular heat of fusion of benzene to be 2.37 kgr.-cal., it follows that the vapour pressure of pure liquid benzene is lowered at this concentration by the ortho compound 24.2 per cent., by the meta 18.9, and by the para 20.2. It will be noticed that, as usual, the freezing point (and vapour pressure) of the water is more depressed by the meta-compound, and that of benzene by the ortho.

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## CCLXXII.—*The Solubility of the Aldehydobenzoic Acids.*

By NEVIL VINCENT SIDGWICK and HERBERT CLAYTON.

THE investigation of the physical properties of this group of substances is of interest in view of the undoubtedly tautomeric behaviour of the ortho-compound. Not only do substitution products of this acid give two series of esters, but the relation of the dissociation constant of the acid itself to those of analogous acids shows that the free acid is largely present in water in an isomeric form (Wegscheider, *Sitzungsber. Akad. Wiss. Wien*, 1905, **104**, IIb, 765). We have therefore examined the solubility of the three isomerides in water and benzene. Although certain peculiarities of these substances prevent a complete investigation, the results are worth recording.

*Preparation of Materials.*—The *o*-aldehydo-acid was prepared by the method of Graebe and Trümpy (*Ber.*, 1898, **31**, 369) by the oxidation of naphthalene to phthalonic acid,\* and the elimination of carbon dioxide from the latter by treatment with sodium bisulphite. The yield in the second stage was found to be increased if the bisulphite compound before acidification was heated for an hour in an oven at  $120^{\circ}$ , instead of being evaporated down on a water-bath as recommended by Graebe and Trümpy. The meta-acid was prepared by several methods: by the partial oxidation of *m*-phthalaldehyde with bromine water (Simonis, *Ber.*, 1912, **45**, 1584), from *m*-toluidine

\* This acid is remarkable for its great solubility in water as compared with organic solvents. At  $15^{\circ}$ , 100 grams of water will dissolve 115 grams of the acid: 100 grams of chloroform, only 2 grams.

through *m*-toluonitrile and its benzylidene chloride (Reinglass, *Ber.*, 1891, 24, 2423), and from *m*-nitrobenzaldehyde through the cyanide. The para-acid was made by the direct oxidation of *p*-toluic acid with manganese dioxide or with chromic acid. None of these methods was found to give a satisfactory yield; and subsequently all three isomerides were prepared with remarkable ease by a method suggested by Dr. W. Dáviés, which will be described in detail in another paper. This consists in the chlorination (up to the benzylidene chloride) of the toluoyl chloride, and the complete hydrolysis of the product.

There is considerable uncertainty in the literature as to the melting points of all these acids. The ortho is stated to melt at 97°. This was found to be the case when it was recrystallised from water, but by solution in benzene and precipitation with light petroleum (b. p. 40–60°) the melting point was raised to 100.5° (corr.). The meta-acid melts according to Reinglass (*loc. cit.*) at 164–166°; according to Simonis (*loc. cit.*) at 175°. We found all pure specimens, however made, to melt at 175° (corr.). Reinglass states that the para-acid begins to melt at 285°, whilst Löw (*Annalen*, 1885, 231, 366) gives the m. p. as 246°, and Simonis as 256°. We found that the high melting point was obtained when the acid had been dried in an oven at about 110° for an hour, but the low one when it had been dried in a desiccator at the ordinary temperature. This suggests that the high melting point may be caused by atmospheric oxidation to terephthalic acid. The acid was therefore separated by extraction with chloroform, and the melting point determined in tubes from which air had been exhausted. Under these conditions the substance, whatever its method of preparation, melted at 248–250° (corr.).

*Determination of Solubility.*—This was carried out in the usual manner, by enclosing weighed quantities of the acid and the solvent in small tubes, which were then sealed. The stable phase in contact with the solution is always the solid; but the ortho-acid, like salicylic acid, gives with water a metastable, two-liquid curve, which at its nearest point is only 4° below the liquid-solid curve. In benzene, the solubilities could not be measured over the whole range, except with the ortho-acid, which offered no difficulties. The meta-acid gave satisfactory results at higher concentrations (above 40 per cent.), but from more dilute solutions a small quantity of a solid separated, which did not dissolve even at the melting point of the acid (175°). At the higher concentrations, this substance was no doubt also formed, but remained in solution. We were not able to determine the nature of this product. It was not isophthalic acid (formed by the oxidation of the aldehyde by the air in the tube), since (1) it was formed to the same extent when the tubes were filled with carbon dioxide, and (2) it was not produced in the experiments with water, although iso-

phthalic acid is almost insoluble in water. It was not an impurity in the original acid, because it was formed, on heating with benzene above 100°, from a sample of the acid which had been dissolved out of a large quantity by benzene at a lower temperature. It must therefore be produced by some reaction of the acid, possibly of the nature of a benzoin condensation. A quantity of the pure acid was heated with benzene at 140° for five hours in an atmosphere of carbon dioxide. From the product the unchanged acid (which is by far the larger part) was removed by extraction with benzene in a Soxhlet apparatus. The insoluble remainder did not melt at 280°, but it could not be obtained in a state pure enough for analysis.

With the *para*-acid in benzene, where the solubilities, owing to the high melting point, are very small, successive determinations with the same tube gave increasing values of the solution temperature, owing, no doubt, to the occurrence of a similar reaction; the values given in the table are those of the first determination in each case, but not much reliance can be placed on them.

The results are given in Tables I and II, and are plotted in Fig. 1 (S-L solid-liquid equilibrium:  $L_1$ - $L_2$  two liquids, the concentrations in both cases being expressed in weights per cent.

TABLE I.  
Solubility in Water.

Ortho.			Meta.		Para.	
Weight per cent.	Temp. S-L.	Temp. $L_1$ - $L_2$ .	Weight per cent.	Temp. S-L.	Weight per cent.	Temp. S-L.
100	100.5°	—	100	175.0°	100	250.0°
91.66	75.0	—	86.76	140.0	79.40	191.5
87.20	64.5	—	81.88	132.9	49.60	181.5
81.50	58.1	—	70.72	121.5	32.46	158.9
59.48	53.2	39.2°	58.87	116.6	19.08	150.9
40.83	51.8	44.0	49.45	114.6	10.24	142.3
29.20	49.9	45.75	40.28	113.5		
20.00	48.92	43.3	29.97	112.3		
9.38	46.1	21.1	19.87	110.7		
			11.22	107.5		
			4.94	99.7		

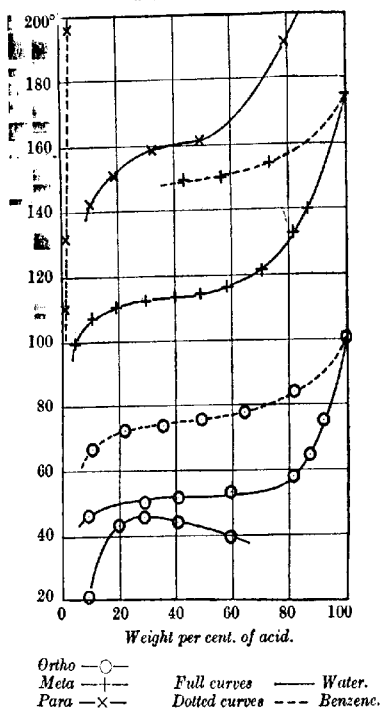
TABLE II.  
Solubility in Benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
100	100.5°	100	175.0°	100	250.0°
81.84	84.0	73.36	154.5	2.40	196.0
64.09	77.8	56.98	149.9	1.41	131.9
49.50	75.7	43.84	149.7	0.96	110.0
35.88	73.9				
21.87	72.3				
10.16	66.7				

*Discussion of Results.*—The solubility curves show that this group of isomerides is undoubtedly abnormal, and also that it has peculiarities of its own. The behaviour with water is in many ways unusual.

FIG. 1.

*Solubility of aldehydobenzoic acids in water and benzene.*



We find, as we do with the hydroxybenzoic and the hydroxytoluic acids (T., 1921, 119, 979), that the ortho-acid alone is capable of forming two liquid layers, although only (as with salicylic acid) in the metastable region. Flaschner and Rankin (*Sitzungsber. Akad. Wiss. Wien*, 1909, 118, IIb, 695) found in such cases an empirical relation between the slope of the curve ( $dc/dt$ , the increase in weight per cent. at the flattest part of the curve for  $1^\circ$  rise in temperature) and the smallest distance in degrees between the two curves, the product of

these two factors being approximately constant. In twelve examples of substituted benzoic acids which they quote, this product  $E$  only varies between 189 and 520, the mean value being 330. *o*-Aldehydebenzoic acid gives the abnormally low value for  $E$  of 76. This may be connected with the tautomeric behaviour of the acid, but the uncertainty makes it impossible to use this quantity to calculate the critical solution temperatures of the other two acids. The curve for the meta-acid is very nearly as flat as that for the ortho, and an attempt was made to supercool the solution to the point of separation into two liquid layers; but this point could not be reached. The values of  $dc/dt$ , the slope of the curve at its flattest, are: ortho 19, meta 15, para 3.4. From the behaviour of other acids of the abnormal type we should expect the meta- and para-curves to have a similar and considerable slope (a small value of  $dc/dt$ ), and the ortho to be much flatter; if the acids were normal, all three curves should have about the same inclination.

The heats of solution in benzene were calculated from the solubility curves, as far as these go, and gave the following results (Table III).

TABLE III.  
Nominal Heats of Solution in Benzene.

Mean mols. per cent.	Heat in kgr.-cal.		Mean mols. per cent.	Heat in kgr.-cal.	
	Ortho.	Meta.		Ortho.	Meta.
95	3.97	7.05	45	32.0	39.7
85	5.83	7.68	35	57.9	128.1
75	8.34	8.68	25	74.9	—
65	12.5	16.1	17.5	62.4	—
55	17.3	22.6	12.5	32.0	—

As we should expect, the increase in the heat of solution is greater for the para-acid; but the difference is unusually small, and the increase for the ortho-acid is much larger than has been observed for any other ortho-substituted benzoic acid in benzene.

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### CCLXXIII.—*The Interaction of Aldehydes or Ketones and Thiocarbamides in the Presence of Acids.* Part II.

By JOHN TAYLOR.

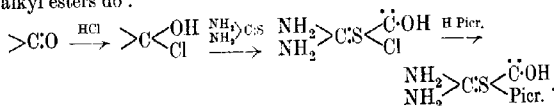
In a previous communication (Dixon and Taylor, T., 1916, 109, 1244), it was shown that thiocarbamides combine, in presence of acids, with formaldehyde and with acetaldehyde to form 'salts.'

4 H\* 2

The mechanism of the reaction appears to be a combination of the aldehyde with the acid followed by union of this compound with the thiocarbamide, a 'salt' of an *S*-substituted thiocarbamide being formed. This salt loses acid on treatment with water, and the resulting base undergoes transformation to an *N*-substituted, non-basic derivative. Condensation follows, either simple internal condensation or a rather complex condensation between two or more molecules. The transformation of *S*-derivative to *N*-derivative is similar to that of compounds of acyl chlorides with thiocarbamides (Dixon and Hawthorne, T., 1907, 91, 122).

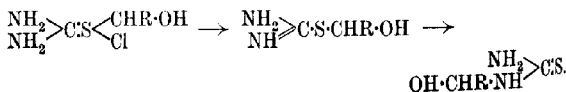
The present communication deals with the combination of aromatic aldehydes and of acetone and of acetophenone with thiocarbamide in presence of acids. Owing to the non-volatility of the combining materials and to the uncertainty of complete interaction, it was not found practicable, in the majority of cases, to isolate the salts as hydrochlorides, but they were obtained as picrates.

When thiocarbamide hydrochloride remains in contact with the aldehyde or the ketone, combination occurs slowly, in some cases weeks being necessary for even partial combination. In general, the products are soluble in water and the addition of picric acid to the solution precipitates the compound as picrate. The reaction follows the course outlined below. Acid leaves the thiocarbamide hydrochloride and combines with the carbonyl group of the aldehyde or ketone (see Taylor, T., 1917, 111, 655); this new compound then unites with thiocarbamide in the same way as the alkyl esters do:

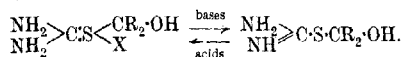


Interaction between thiocarbamide and aldehyde or ketone may also be brought about by adding to the mixture of the components hydrogen chloride gas, sulphuric acid, or phosphoryl chloride. As before, the compounds may be isolated readily as picrates.

When the combined acid was withdrawn from the compounds with the aldehydes, non-basic condensation products were formed, somewhat similar to those produced with acetaldehyde; the aldehyde residue, being acidic in character, migrates from sulphur to nitrogen:



When acid was withdrawn from the compound with acetone, an easily decomposable basic product was left, from which a picrate, similar to that obtained from the original material, may be obtained. The formation of mercaptoid decomposition products shows that the acetone residue remains attached to sulphur. The ketone residue, being less acidic than the aldehyde residue, behaves like an alkyl group :



#### EXPERIMENTAL.

*Thiocarbamide and Benzaldehyde.*—The solid obtained by keeping a mixture of equal weights of thiocarbamide hydrochloride and freshly distilled benzaldehyde was extracted, after two days, with water, in which it was only partly soluble. Picric acid gave with the filtrate a viscous picrate which, after crystallisation from alcohol, melted at 144–146°. This was an impure product, the percentage of sulphur being about 5.4 (thiocarbamide–benzaldehyde picrate,  $\text{C}_{14}\text{H}_{13}\text{O}_8\text{N}_3\text{S}$ , requires S = 7.78 per cent.).

The portion of the product sparingly soluble in cold water appears to be formed by condensation of benzaldehyde with thiocarbamide. After recrystallisation from hot water or from alcohol, it decomposed at 176–177° (Found : S = 19.7. The condensation product,  $\text{C}_8\text{H}_8\text{N}_2\text{S}$ , requires S = 19.5 per cent.). The condensed material showed no sign of recombining with acid, hence it was no longer an *S*-substituted derivative. Its comparatively low melting point suggests that the molecule is simple. A similar result ensued when a mixture of benzaldehyde and thiocarbamide was attacked by phosphoryl chloride, a pure picrate not being obtained. Sulphuric acid is a slow combining reagent. When a mixture of the components, which had been kept for four days, was extracted with ether, the residue proved to be thiocarbamide sulphate.

*Thiocarbamide and Salicylaldehyde.*—Thiocarbamide hydrochloride and salicylaldehyde combine exceedingly slowly and imperfectly, but after four months the mixture almost entirely dissolved in water. The solution yielded a picrate easily soluble in alcohol but insoluble in water. Phosphoryl chloride effected a considerable amount of combination in two days. When the mixture was treated with water, part dissolved leaving a residue of flocculent solid and pasty material, and from the solution a picrate was obtained, which, after crystallisation from alcohol, decomposed at 166–168° (Found : S = 7.6. Thiocarbamide–salicylaldehyde picrate,  $\text{C}_{14}\text{H}_{13}\text{O}_9\text{N}_3\text{S}$ , requires S = 7.5 per cent.).



The pasty material, on continued treatment with water, gradually hardened to form the flocculent solid already mentioned. This is apparently a complex condensation product [Found:  $S = 10.8$ . A simple condensation of thiocarbamide (1 mol.) with salicylaldehyde (1 mol.),  $C_8H_8ON_2S$ , requires  $S = 17.8$ , whilst a condensation of thio-carbamide (1 mol.) with salicylaldehyde (2 mols.),  $C_{16}H_{14}O_3N_2S$ , requires  $S = 10.6$  per cent.]. Its reluctance to fusion—it does not melt when heated to  $205^\circ$ —is compatible with the more complex structure.

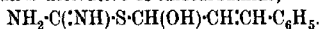
An analogous compound was obtained from thiocarbamide and acetaldehyde (Dixon and Taylor, *loc. cit.*, p. 1251).

*Thiocarbamide and Cinnamaldehyde.*—On mixing equivalent quantities of thiocarbamide hydrochloride and cinnamaldehyde, heat was developed, and after three or four days an impure, viscous, brown additive product obtained. Addition of an alcoholic solution of picric acid to the substance, dissolved in alcohol, gave a crystalline picrate, which, after recrystallisation from hot alcohol, melted at  $184^\circ$  (Found:  $S = 7.48$ . Thiocarbamide-cinnamaldehyde picrate,  $C_{16}H_{16}O_6N_2S$ , requires  $S = 7.32$  per cent.).

Thiocarbamide-cinnamaldehyde sulphate was obtained more readily. To a mixture of thiocarbamide and a slight excess of cinnamaldehyde was added concentrated sulphuric acid (1 equiv.) with continual stirring, when the whole mass became solid. On boiling with alcohol, the sulphate, which was sparingly soluble, was left as a white, apparently amorphous powder. It is sparingly soluble in cold water, the solution being neutral and affording the usual reactions of sulphates. Boiling water decomposes the compound to some extent, liberating cinnamaldehyde. Addition of picric acid to either aqueous or alcoholic solutions gave the same picrate as before. The sulphate decomposed at  $171$ – $173^\circ$  [Found:  $S = 18.6$ . Thiocarbamide-cinnamaldehyde sulphate,  $(C_{10}H_{11}ON_2S)_2 \cdot H_2SO_4$ , requires  $S = 18.6$  per cent.].

When the sulphate is triturated with ammonia, a cream-coloured base is formed which, after being washed with water, decomposed at  $122^\circ$  (Found:  $S = 15.1$ . Thiocarbamide-cinnamaldehyde,  $C_{10}H_{12}ON_2S$ , requires  $S = 15.3$  per cent.). The base dissolved readily in alcohol, and its solution gave the same picrate (mixed melting-point method) as that obtained from the sulphate. The formation of the simple basic additive compound instead of the non-basic condensation product was unexpected. After keeping for a week, no marked change was perceptible. A slowly transformable, basic aldehyde additive compound of thiocarbamide has previously been prepared from thiocarbamide hydrochloride and an alcoholic solution of acetaldehyde (Dixon and Taylor, *loc. cit.*,

p. 1252). This lost its basic properties within a week. The new compound appears to be quite stable. Its basic properties show that it remains an *S*-derivative of thiocarbamide,



*Thiocarbamide and Acetone.*—Thiocarbamide hydrochloride and acetone combine very slowly. If dry acetone be used, scarcely any sign of combination, as shown by the formation of a picrate, will be evident after ten days, but with moist acetone three days are sufficient for interaction to be detected. When hydrogen chloride is passed into a solution of thiocarbamide in acetone, a copious precipitate of thiocarbamide hydrochloride is obtained. The mother-liquors, after keeping for three or four days, yield a good crop of thiocarbamide-acetone picrate. Thiocarbamide hydrochloride, kept in contact with acetone for three months, slowly changes. At first it dissolves, then, as the acetone slowly evaporates, hexagonal plates separate from solution. These melt at  $191\text{--}192^\circ$ , with previous softening, and are readily soluble in water, giving a neutral solution from which is obtainable the same picrate as before.

Phosphoryl chloride or phosphorus trichloride much more quickly brings about combination between thiocarbamide and acetone. The addition of phosphoryl chloride to mixtures which had given no picrate after three days caused the formation of picrate after four or five hours. This picrate was free from phosphorus and was identical with the picrates obtained from the other sources. After three or four recrystallisations from alcohol, it decomposed at  $193\text{--}194^\circ$  (Found: S = 8.37; N = 19.31. Thiocarbamide-acetone picrate,  $\text{C}_{10}\text{H}_{13}\text{O}_8\text{N}_5\text{S}$ , requires S = 8.81; N = 19.28 per cent.). Distilled with aqueous sodium hydroxide, the picrate yielded a distillate having the odour of acetone and responding to Reynolds's test (*Z. anal. Chem.*, 1885, **24**, 147) and to Egeling's nitroprusside test for acetone (*Chem. Zentr.*, 1894, ii, 457).

An interesting isomeride of this picrate was obtained from a mixture of thiocarbamide hydrochloride with little more than its equivalent of acetone which had been kept in a sealed vessel for about two years. This picrate was scarcely soluble in alcohol and melted at  $149\text{--}151^\circ$  (Found: S = 8.61; N = 18.90 per cent.). The two picrates thus differ sharply.

An attempt to obtain the free base was only partly successful. Thiocarbamide, acetone, and phosphoryl chloride were kept together for three days, water was then added, and sodium carbonate until the liquid was alkaline. A slight oily precipitate was filtered off, the clear liquid allowed to evaporate to dryness, the residue extracted with chloroform, and the solvent evaporated,

when a clear, gummy residue was obtained. This, being very unstable, was not analysed. That it was an *S*-derivative of thiocarbamide was shown by its yielding substances with mercaptoid odours and by its solution in dilute hydrochloric acid giving the same picrate as that already obtained from other preparations. Thus the acetone residue does not migrate to the nitrogen atom when the acid is removed.

*Phenylthiocarbamide and Acetone*.—A solution of phenylthiocarbamide in acetone was saturated with hydrogen chloride, and after twelve hours water was added until oil appeared. This was filtered off and portions of the filtrate were treated with aqueous and with alcoholic solutions of picric acid. The picrates thus obtained were apparently identical and sparingly soluble in alcohol. After thorough extraction with alcohol, the picrate melted at 190–191° (Found: S = 6.71; N = 14.72. Phenylthiocarbamide-acetone picrate,  $C_{16}H_{17}O_8N_3S$ , requires S = 7.29; N = 15.9 per cent.).

*Thiocarbamide and Acetophenone*.—To an excess of acetophenone, thiocarbamide was added, phosphoryl chloride was run into the mixture until reaction was no longer apparent, and the mixture was heated for about ten minutes on a water-bath. The resulting mixture of paste and liquid was filtered, the paste dissolved in just sufficient alcohol, and ether added. The precipitated salt was washed with ether and dissolved in alcohol, and from the solution the picrate was precipitated by the addition of alcoholic picric acid, followed by water. An emulsion was first formed which presently solidified. After crystallisation from alcohol, the picrate melted at 168–174°, the temperature of fusion depending on the rate of heating (Found: S = 7.64. Thiocarbamide-acetophenone picrate,  $C_{15}H_{15}O_8N_3S$ , requires S = 7.52 per cent.).

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## CCLXXIV.—*Intermetallic Actions. The System Aluminium-Arsenic.*

By QASIM ALI MANSURI.

THE action of arsenic on aluminium appears to be mentioned only in *Compt. rend.*, 1900, 130, 1391, where it is stated that arsenic combines with aluminium at high temperatures, but nothing is recorded about the exact nature of the compounds. To throw further light on this problem, it was therefore considered necessary

to make a complete investigation of this system. Aluminium of 99.6 per cent. purity, as determined by the hydrogen method, and resublimed arsenic were used.

#### EXPERIMENTAL.

*Preliminary Work.*—The chief experimental difficulty met with was due to the volatile nature of arsenic. Attempts were therefore made to prepare the alloys in sealed glass tubes, under a seal of molten potassium sulphate (in which the crucible containing a mixture of aluminium and arsenic was dipped, and the sulphate was allowed to freeze on top of it to form a seal), and by blowing or passing arsenic vapour through or over molten aluminium heated at a high temperature.

It was noticed that no action takes place between arsenic and aluminium up to about 600°. Even at about 750° the metals do not react with each other if the pressure of arsenic vapour is too high (about one atmosphere). At low pressure and high temperature, probably yellow arsenic is formed, and it is this which reacts with aluminium. At about 800° and at low pressure, this action is more marked, the yellow arsenic forming a brown compound,  $\text{Al}_3\text{As}_2$ , with aluminium which does not melt at that temperature nor dissolve in molten aluminium. At atmospheric pressure, this action takes place at about 900°, with the same result.

The view that it is yellow arsenic which reacts chemically with aluminium, and not the black variety, is supported by the fact that whilst, in the favourable circumstances mentioned above, no black arsenic was left, there was always a little yellow coating in the upper part of the tubes. Again, the product of the dissociation of the compound is yellow arsenic. The inner surfaces of the stoppered bottles in which the alloys were stored were always found covered with a deposit of yellow arsenic, which turned to the brown variety after exposure to light for some time. The brown compound is stable at high temperatures, for when freshly formed it does not give off arsenic vapour even at 1000°, but when it is cooled and kept for some time and heated again, it begins to evolve arsenic vapour at about 500°. Also, when freshly prepared, the compound dissolves almost completely in dilute hydrochloric acid, but after keeping for some time at room temperature, it becomes darker, and on treatment with dilute hydrochloric acid there is always a black residue of almost pure arsenic. These facts show that the compound is stable at high temperatures, but breaks up at low temperatures.

*Systematic Investigation of the System.*—After the preliminary

observations, mentioned above, for the determination of the *liquidus* at the aluminium end of the equilibrium diagram, it was necessary to heat the brown compound isolated, with aluminium at a very high temperature out of contact with air, as at low temperatures the solid compound separated out from molten aluminium almost completely. It is possible that at very high temperatures the compound may melt and may then be miscible with molten aluminium, but this suggestion could not be tested owing to lack of suitable heating apparatus. However, to throw some light on this point, work was started in sealed hard-glass tubes.

*Thermal Analysis.*—As hard-glass tubes become porous to arsenic vapour at about  $650^{\circ}$ , a platinum couple could not be used. After testing several base-metal couples, the author found a couple made of two chrome-nickel wires of different compositions most suitable for working with arsenic alloys, as it was not easily contaminated with arsenic and could be used satisfactorily up to about  $1100^{\circ}$ . The two wires (No. 25 B.S.G.), containing different percentages of chromium, formed a couple about twice as sensitive as a platinum-rhodium couple. Two chrome-nickels differing even more in composition should form a still more sensitive couple.

Close contact of the hot junction of the couple with the outside of the glass tubes in which the alloys were prepared, was made by means of purimachos cement. Used in this way, the couple was quite sensitive, and all thermal changes in the alloys could be easily detected.

As the alloys were heated by means of a gas tube-furnace, the heating could not be made very regular and therefore the heating curves of the alloys could not be obtained.

The cooling curves were obtained by means of a water-dropping curve tracer. In this arrangement, a suspended mirror-galvanometer throws a spot of light on a glass screen, which is moved vertically by means of a simple water-dropping arrangement. The spot of light moves horizontally as the temperature changes, and thus a curve is traced, by means of a soft pencil, on a paper mounted on the glass screen. A millivoltmeter was arranged in series with the galvanometer, so that when a break occurred on a curve on the tracer, a reading corresponding with it could be taken on the millivoltmeter. The couple was calibrated by means of tin, lead, zinc, aluminium, commercial antimony, m. p.  $622^{\circ}$ , level, and copper.

Cooling curves of the alloys were traced from about  $750^{\circ}$ . Alloys containing up to 5 per cent. of arsenic melted satisfactorily, but when 7 per cent. of arsenic had been added, the pieces of aluminium did not fuse together, but remained separate, and were coated with

the brown compound; nevertheless, a thermal arrest occurred at the freezing point of aluminium. It seems that in these alloys the brown compound forms a strong and hard envelope round the aluminium which holds molten aluminium within it and does not allow it to run together even although the tubes are well shaken.

In alloys containing up to 10 per cent. of arsenic no thermal arrest could be detected at the higher temperatures. The only thermal arrest observed was at the freezing point of aluminium and therefore the determination of the *liquidus* had to be postponed.

In order to find the composition of the compound thermally, 12 grams of aluminium turnings and 1.5 grams of arsenic were heated at 750° in a sealed, evacuated (about 15 mm. pressure) hard-glass tube. (It was noticed in preliminary work that in a glass tube about 6 inches in length and half an inch in diameter about 2 grams only of arsenic could be converted at one time to yellow arsenic, under the experimental conditions, and made to combine with aluminium.) The aluminium turnings, thus coated with the compound, were again mixed with 1.5 grams of arsenic and again heated in another glass tube to the same temperature. In this way, the compound could be gradually prepared. Each time a cooling curve was also taken. The only thermal arrest observed in all these cases was at the freezing point of aluminium, and this became smaller and smaller, in accordance with and proportional to the eutectic times law, until, with the alloy containing about 64 per cent. of arsenic, it could no longer be detected.

An attempt was next made to prepare alloys containing higher percentages of arsenic in the same way by the gradual addition of arsenic to the compound, but without success; arsenic separated in the upper part of the glass tube, and the brown compound remained in the lower part. This result showed that the compound did not alloy even with arsenic and that no other compound of a higher composition was formed. Had the brown compound alloyed with arsenic and formed a eutectic, a thermal arrest should have been observed at some temperature up to 750°.

When aluminium turnings were heated at about 900° with arsenic vapour in an atmosphere of nitrogen, an alloy containing at most about 69 per cent. of arsenic was formed. This alloy also did not melt and appeared similar to the brown compound prepared by the other methods.

*Chemical Analysis.*—The arsenic in alloys rich in aluminium was estimated iodometrically by Hefti's method ("Analytical Chemistry," Treadwell and Hall, 1905, II, p. 214).

The solution of aluminium chloride having been filtered to remove

the small residue of silica, the aluminium in the filtrate was estimated gravimetrically as  $\text{Al}_2\text{O}_3$ .

In the alloys rich in arsenic, it seems that the compound breaks up on keeping at low temperatures, and the black arsenic formed is not attacked by dilute hydrochloric acid. The arsenic in these alloys was therefore first converted to arsenic acid and then estimated by Williamson's method.

For the estimation of aluminium, 100 c.c. of the solution remaining after the estimation of arsenic were filtered, so boiled with concentrated hydrochloric acid and potassium bromide as to ensure removal of arsenic, and the aluminium was then estimated gravimetrically as above.

These methods gave good results, as is shown by the duplicates recorded below:

(a) Filings obtained from the outer surface of the alloy containing 5 per cent. of arsenic: Found, Al = 91.74; As = 7.85;  $\text{SiO}_2$  = 0.27 per cent.

(b) Filings obtained from the same alloy after filing off about 1 mm. of the outer surface: Found, Al = 99.29; As = 0.31;  $\text{SiO}_2$  = 0.22 per cent.

(c) Alloy containing 7.5 per cent. of arsenic, after filing off the outer surface: Found, Al = 98.95; As = 0.58;  $\text{SiO}_2$  = 0.19 per cent.

(d) Alloy heated with the compound in the oxy-hydrogen flame; after filing off the outer surface: Found, Al = 98.01; As = 1.11;  $\text{SiO}_2$  = 0.29 per cent.

(e) The compound  $\text{Al}_3\text{As}_2$  as prepared in glass tubes, after powdering and passing through a 120-mesh sieve: Found, Al = 34.81, 34.93; As = 64.57, 64.39;  $\text{SiO}_2$  = 1.2, 0.9 (theoretically, As = 64.88 per cent.).

(f) The same alloy, without powdering: Found, Al = 35.00; As = 63.64;  $\text{SiO}_2$  = 1.03 per cent.

(g) The compound  $\text{Al}_3\text{As}_2$  as prepared by submitting aluminium filings to the action of arsenic vapour in an atmosphere of nitrogen at about  $900^\circ$ : Found, Al = 31.21, 30.74; As = 69.00, 69.17;  $\text{SiO}_2$  = 0.23, 0.21 per cent.

*Micrographic Analysis.*—As the compound  $\text{Al}_3\text{As}_2$  did not melt at the temperature of the experiments, it was simply mixed with aluminium in all the alloys and was in an amorphous, powdery condition. Such heterogeneous alloys were very difficult to polish and even on polishing they did not show any uniform and regular structure except where the compound had been acted upon by moisture and decomposed, making a few blow-holes. No successful photomicrographs of the alloys could therefore be taken.

*Conclusions.*

1. Aluminium and arsenic combine to form the compound  $\text{Al}_3\text{As}_2$ —as shown by thermal and chemical analysis. The action commences at about  $750^\circ$  and a low pressure, where yellow arsenic is formed and acts upon the aluminium.

2. The compound  $\text{Al}_3\text{As}_2$  is stable at high temperatures, but begins to break up at lower temperatures. When the compound breaks up, yellow arsenic is first formed.

3. The compound  $\text{Al}_3\text{As}_2$  is a brown, amorphous powder which looks like iron rust and does not melt up to the temperature of fusion of silica (about  $1600^\circ$ ).

4. It is very reactive and evolves arsenic trihydride freely when exposed to moisture. For this reason, the alloys were always stored in stoppered bottles, and all polishing, etc., was done in fume chambers.

5. When heated in air, the compound oxidises to alumina and arsenious oxide.

6. The solid compound does not seem to dissolve in molten aluminium to any appreciable extent, but separates from it almost completely at its freezing point, nor does it alloy with arsenic to form a eutectic. The equilibrium diagram of the system is probably like that of the system aluminium-antimony investigated by Tammann (*Z. anorg. Chem.*, 1906, **48**, 53). It attains an abnormal or a flat (showing immiscibility) maximum at very high temperature and has for its *solidus* the horizontals corresponding to the melting points of aluminium and arsenic, respectively.

7. It is interesting to note that most of the compounds of arsenic with other metals are also of the type  $\text{M}_3\text{As}_2$ , as, for example,  $\text{Cd}_3\text{As}_2$  (*Z. Metall.*, 1913, **4**, 228),  $\text{Hg}_3\text{As}_2$  (*Arch. Pharm.*, 1899, **237**, 126),  $\text{Sn}_3\text{As}_2$  (*Gazzetta*, 1912, **42**, I, 274; *Atti R. Accad. Lincei*, 1911, [vi], **20**, 593),  $\text{Fe}_3\text{As}_2$  (*Metallurgie*, 1907, **4**, 131),  $\text{Zn}_3\text{As}_2$  (*Z. anorg. Chem.*, 1921, **118**, 264),  $\text{Mn}_3\text{As}_2$  (*Metallurgie*, 1911, **8**, 727),  $\text{Co}_3\text{As}_2$  (*ibid.*, 1908, **5**, 150),  $\text{Ni}_3\text{As}_2$  (*ibid.*, 1907, **4**, 207), and  $\text{Mg}_3\text{As}_2$  (compound obtained by Parkinson in 1867).

The author is very much indebted to Mr. C. T. Heycock for his valuable advice and sympathetic guidance throughout the work.

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CCLXXV.—*The Reversibility of the Reaction between Nitrogen, Carbon, and Sodium Carbonate.*

By CHRISTOPHER KELK INGOLD and DANIEL WILSON.

At temperatures above  $850^{\circ}$  (the m. p. of sodium carbonate), the system  $\text{N}_2 + 4\text{C} + \text{Na}_2\text{CO}_3 = 3\text{CO} + 2\text{NaCN}$  has three phases, —a gaseous phase consisting principally of nitrogen and carbon monoxide; a liquid phase, chiefly composed of sodium carbonate and sodium cyanide; and solid carbon. It follows that, for a given temperature and pressure, the composition of the gaseous phase will determine that of the liquid phase, and vice versa. Further, since the heat of the reaction is  $-238,000$  cals., the relationship between the compositions of the liquid and gaseous phases must change rapidly with changing temperature; and, since the reaction is accompanied by a large change in volume, pressure must also have a marked effect.

The law of mass action, when applied to the gaseous phase of the reaction under consideration, gives, for a constant temperature, the relation

$$\frac{[\text{NaCN}]^2[\text{CO}]^3}{[\text{Na}_2\text{CO}_3][\text{C}][\text{N}_2]^2} = K. \quad \dots \quad (i)$$

This admits of reduction to a form in which the variables are capable of direct measurement if certain suppositions be made, of which the following are the most important:

(i) That the gas laws can be applied to the vapours of carbon, sodium carbonate, and sodium cyanide at the temperatures employed.

(ii) That the (partial) vapour pressures of sodium carbonate and sodium cyanide in the space above the mixed liquids are linear functions of the molecular concentrations of each in the liquid phase.

(iii) That the vapour pressures of carbon, sodium carbonate, and sodium cyanide are negligible in comparison with the total pressure.

The truth of the third supposition has been verified by direct experiment. Sodium cyanide is by far the most volatile of the three substances, but its vapour pressure at the temperatures employed is sufficiently small to guarantee the truth both of the first and third assumptions to an approximation of about 1 per cent. The second assumption is an application of a general rule, which usually holds fairly accurately for mixtures of non-associated liquids, and has been verified as regards sodium cyanide in mixtures of sodium cyanide and sodium carbonate by a direct determination

of the total pressure curve. This is a straight line passing through the sodium carbonate origin.

Equation (i) becomes

$$\frac{x^2}{1-x} \cdot \frac{(1-p)^3}{p} = K' \quad \dots \quad (ii)$$

where  $x$  is the proportion of the combined sodium which is present in the liquid phase as sodium cyanide (that is, the yield of sodium cyanide reckoned as a fraction of the theoretical), and  $p$  is the partial pressure of nitrogen calculated as a fraction of the total pressure of nitrogen and carbon monoxide, which is supposed for the present to be always the same, namely, one atmosphere.  $K'$  is a derived constant:

$$K' = K \cdot p_{\text{Na}_2\text{CO}_3} \cdot p_{\text{C}}^4 / p_{\text{NaCN}}^2,$$

where  $p_{\text{Na}_2\text{CO}_3}$ ,  $p_{\text{C}}$ , and  $p_{\text{NaCN}}$  are the saturated vapour pressures of pure sodium carbonate, pure carbon, and pure sodium cyanide at the temperature to which equations (i) and (ii) apply. Hence

$$\log_e K' = \log_e K + \log_e p_{\text{Na}_2\text{CO}_3} + 4 \log_e p_{\text{C}} - 2 \log_e p_{\text{NaCN}}.$$

For different temperatures within an interval which is not too great in comparison with the absolute temperature, the heat of the reaction, and the latent heats of vaporisation of sodium carbonate, carbon, and sodium cyanide may be treated as constants, so that each of the four terms on the right-hand side of the last equation should vary linearly with the reciprocal of the absolute temperature. This follows from the integration of the reaction isochore and the vapour pressure equation of Clausius and Clapeyron. Hence, by addition of the terms,

$$\log_e K' = a + b/T,$$

and, combining with equation (ii),

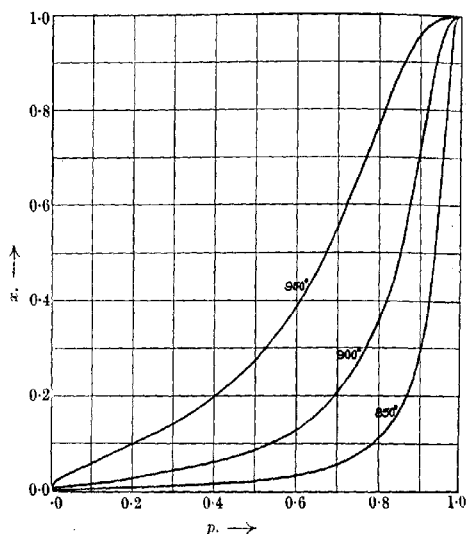
$$\log_{10} \left\{ \frac{x^2}{1-x} \cdot \frac{(1-p)^3}{p} \right\} = \alpha + \frac{\beta}{T} \quad \dots \quad (iii)$$

where  $\alpha$  and  $\beta$  are constants, which have to be determined by experiment. Equation (iii) should therefore represent the experimental results to a degree of approximation of the order of 1 per cent. in  $x$  or  $p$ , which is equivalent to about  $2^\circ$  in  $T$ . This is approximately the degree of accuracy of the measurements themselves (*vide* experimental part). The form of the function represented by equation (iii) is shown by the curves in the diagram, on which  $x$  is plotted against  $p$  for the three temperatures  $850^\circ$ ,  $900^\circ$ , and  $950^\circ$ .

The equilibrium in question has been examined by Ferguson and Manning (*J. Ind. Eng. Chem.*, 1919, **11**, 946), whose results, expressed

in isothermals connecting the compositions of the gaseous and liquid phases, are in marked conflict with the requirements of the theoretical formula (equation iii), a fact which seems to have escaped the notice of the authors. Nevertheless, the disagreement is immediately evident from the form of their curves, which differ markedly from those in the accompanying diagram. Equation (iii), however, correctly represents the results recorded in this paper, and there can be little doubt that the principal error affecting Ferguson and Manning's determinations arises from the volatility

FIG. 1.



of sodium cyanide, a considerable proportion of which must have escaped from the reaction mixture under the conditions they employed.

The values of the fundamental constants are found to be  $\alpha = 23.91$ ,  $\beta = -31180$ . From these numbers, the following table of values of  $100x$  has been calculated for temperatures within the experimental range. Excepting in the immediate neighbourhood of the limits of the system, intermediate values may be obtained by linear interpolation, although the last figure will not invariably have its full significance. In interpreting the table it is to be remembered that  $p$  is the partial pressure of nitrogen when the

combined pressures of nitrogen and carbon monoxide amount to one atmosphere. The total pressure, however,\* will be a little more than one atmosphere owing to the formation of carbon dioxide by the reversible reaction,  $2\text{CO} = \text{CO}_2 + \text{C}$ . It follows, also, that if a mixture containing  $p'$  per cent. of nitrogen and  $100-p'$  per cent. of carbon monoxide be admitted to the reaction mixture,  $p$  will be a little greater than  $p'/100$ , because (a) a certain amount of carbon monoxide will be destroyed, the proportion depending both on its temperature and partial pressure, (b) this reaction involves a diminution in volume. The calculation of  $p$  from  $p'$  can easily be made with the aid of Rhead and Wheeler's data for the equilibrium,  $2\text{CO} = \text{CO}_2 + \text{C}$  (T., 1911, 99, 1140). The differences between  $p$  and  $p'/100$  are for the most part less than 2 per cent.

100p.	850°.	860°.	870°.	880°.	890°.	900°.	910°.	920°.	930°.	940°.	950°.
0.5	0.1	0.2	0.2	0.3	0.4	0.4	0.5	0.7	0.8	1.0	1.2
1.0	0.2	0.3	0.3	0.4	0.5	0.6	0.7	0.9	1.1	1.4	1.7
2.0	0.3	0.4	0.4	0.5	0.7	0.8	1.0	1.3	1.6	2.0	2.4
5.0	0.4	0.5	0.6	0.8	0.9	1.0	1.4	1.8	2.4	3.1	4.0
10.0	0.5	0.6	0.8	1.0	1.3	1.6	2.1	2.6	3.5	4.5	5.8
15.0	0.6	0.8	1.1	1.4	1.7	2.2	2.9	3.6	4.7	6.0	7.7
20.0	0.8	1.1	1.4	1.8	2.3	2.9	3.7	4.7	5.9	7.6	9.7
25.0	1.0	1.4	1.7	2.2	2.8	3.6	4.5	5.7	7.2	9.1	11.8
30.0	1.2	1.7	2.1	2.7	3.4	4.2	5.4	6.8	8.6	11.0	14.0
35.0	1.4	1.9	2.4	3.2	4.0	5.1	6.4	8.0	10.4	13.2	16.7
40.0	1.6	2.2	2.8	3.7	4.8	6.1	7.7	9.8	12.3	15.8	19.7
45.0	1.8	2.5	3.3	4.3	5.7	7.2	9.1	11.6	14.8	18.7	23.4
50.0	2.2	3.1	4.0	5.3	6.7	8.6	11.1	14.0	17.7	22.2	27.6
55.0	2.7	3.8	4.9	6.4	8.1	10.5	13.4	16.7	20.9	26.3	32.4
60.0	3.5	4.7	6.1	7.9	10.2	13.1	16.5	20.7	25.8	31.8	38.7
65.0	4.6	6.0	7.8	10.0	13.0	16.3	20.5	25.5	31.4	38.4	46.3
70.0	5.8	7.6	9.8	12.8	16.4	21.0	26.0	32.2	39.2	47.0	55.7
75.0	8.0	10.4	13.4	17.0	21.5	27.3	33.6	40.9	48.7	57.4	66.1
80.0	11.4	14.5	18.4	23.7	29.4	36.4	44.0	52.4	60.8	69.5	77.3
85.0	17.1	22.1	27.6	34.9	41.8	50.1	58.8	67.4	76.0	83.2	88.5
90.0	29.8	37.4	45.3	54.7	63.4	72.0	80.0	86.0	90.2	93.7	96.0
95.0	63.6	71.8	79.5	86.5	91.0	94.3	96.6	98.0	98.7	99.3	99.5
98.0	97.2	97.8	98.2	98.7	99.2	99.6	99.8	99.8	100.0	100.0	100.0
99.0	99.4	99.6	99.7	99.8	100.0	100.0	100.0	100.0	100.0	100.0	100.0
99.5	99.5	99.9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

In view of the general agreement of the experimental results with the requirements of the law of mass action, there can be little doubt that the complete equation

$$\log_{10} \left\{ \frac{x^2}{1-x} \cdot \frac{(1-p)^3}{p} \cdot \pi^2 \right\} = 23.91 - \frac{31180}{T}$$

( $\pi$  stands for the total pressure of nitrogen and carbon monoxide) represents the behaviour of the system under discussion over a wide range of variables, despite the fact that the applicability of this equation has not yet been verified experimentally for different total (as distinguished from different partial) pressures.

## EXPERIMENTAL.

The general plan of these experiments consisted in passing a mixture of carbon monoxide and nitrogen of known composition over a boat containing weighed quantities either of sodium carbonate and carbon, or of sodium cyanide, together with a catalyst (iron), the total pressure of the gas, and the temperature of the boat and its contents, being known and constant. The composition of the equilibrated liquid phase was then determined by rapidly cooling and analysing the product in the boat.

## A.—Materials.

*Nitrogen and Carbon Monoxide.*—Nitrogen taken from a cylinder, and carbon monoxide prepared from sodium formate and sulphuric acid were mixed over water in the required proportions, and freed from traces of carbon dioxide, oxygen, and water vapour by passage through sodium hydroxide, alkaline pyrogallate, and sulphuric acid, before sampling for analysis, and admitting to the reaction tube.

*Sodium Carbonate, Carbon, and Iron.*—The usual procedure was to approach the equilibrium from both sides. When sodium carbonate and carbon were the starting materials, the iron was introduced in the form of ferric oxide, which quickly became reduced to metallic iron by the carbon monoxide in the gaseous mixture. The suitability of these materials was controlled by replacing ferric oxide by ferric acetate, and by complete analyses of the final products. It was thus proved that the formation of cyanates was inappreciable, although the aqueous lixiviate was frequently contaminated with traces of sodium hydroxide. These were of the order of 1 per cent. of the total alkali, and appeared to be roughly proportional to the oxygen introduced in combination with iron.

*Sodium Cyanide and Iron.*—When sodium cyanide was to be the starting point, the material actually used was sodium ferrocyanide, which decomposed quantitatively, at the temperature employed, into sodium cyanide, iron, carbon, and nitrogen, the iron being in a very active condition. The lixiviates from these experiments contained no trace either of sodium cyanate or of sodium hydroxide. Experiments with 98 per cent. sodium cyanide and iron, added in the form of oxide, yielded the usual small amount of sodium hydroxide on lixiviation together with detectable quantities of cyanate. These materials were therefore rejected in favour of sodium ferrocyanide.

## B.—Apparatus.

*Furnace.*—Heating was accomplished by means of a Haras tube furnace consisting of a platinum ribbon wound on an unglazed

porcelain tube of 3 cm. bore and bedded in well-burnt magnesia. The winding was spaced in such a way as to give a constant temperature over a distance of about 8 cm. in the centre of the tube. The insulation (asbestos) was such that a current of 3.2 amperes maintained a steady temperature of  $900^{\circ}$  at the centre, the resistance of the ribbon at this temperature being 24 ohms. A current of 5 amperes raised this temperature from  $500^{\circ}$  to  $900^{\circ}$  in fourteen minutes.

*Reaction Tube.*—This was of glazed porcelain, was lined with thin sheet nickel, and had a bore of 21 mm. It was inserted through the furnace, and connected at one end with the gas supply system, and at the other with a water-jacketed silica extension tube, of the same diameter, which was used for rapidly cooling the boat. The other end of the silica tube was joined to a glass tube, also of the same diameter, which communicated through a side tube with a sampling trough, a gas reservoir, and a mercury pump.

*Reaction Boat.*—This was of iron, 5 cm. long and as capacious as possible within the limits of its length and the size of the reaction tube. It was welded to a polished iron rod, 3 mm. in diameter, which served as a handle, and passed through a gas-tight, graphite-lubricated rubber bung in the end of the glass extension tube. The latter was just long enough to prevent the bung from being burned by the rod when the boat was withdrawn from the centre of the furnace to the silica cooling tube.

*Thermometer.*—Temperatures were measured just outside the reaction tube by means of a platinum-rhodium couple standardised on the melting points of sodium chloride ( $800^{\circ}$ ), sodium sulphate ( $384^{\circ}$ ), and potassium sulphate ( $1063^{\circ}$ ). The readings were corrected for the small temperature gradient through the walls of the tube, and the values recorded below for the temperatures of the reaction mixture are believed to be accurate to within  $2^{\circ}$ .

#### C.—Method.

A weighed charge of the intimately mixed starting materials was placed in the boat, which was kept in the silica tube while the temperature of the furnace was adjusted, and the air in the reaction tube replaced by a mixture of nitrogen and carbon monoxide in the required proportions. The water-overflow of the gas reservoir which was to receive the out-going gases was adjusted to a level such that the total pressure of nitrogen and carbon monoxide in equilibrium with carbon and carbon dioxide at the temperature chosen would amount to 760 mm. of mercury (p. 2281). The boat was then pushed up to the reaction zone and the gas passed in a steady stream. The incoming gas was sampled for analysis at

the beginning and at the end of the experiment, and the out-going gases every thirty minutes during its progress, the completion of the process being indicated by the constancy of their composition. The temperature was read every few minutes and kept as closely as possible to the required value. At the end of the operation, the reaction tube was closed by glass stop-cocks, and the boat withdrawn to the water-jacketed silica tube. A few minutes later, the reaction tube was completely evacuated by means of the mercury pump, and the gas thus obtained analysed. The product in the boat was analysed for cyanide, carbonate, total alkali, and occasionally for ferrocyanide (which was never present) and cyanate (see p. 2282). The gas collected in the reservoir was also analysed.

#### D.—*Reduction of the Results.*

*Gas Analysis.*—The composition of the last few samples of out-going gas was found to differ from that of the in-coming gas by an amount which was the same as that calculated from Rhead and Wheeler's data for the reaction  $2\text{CO} = \text{C} + \text{CO}_2$  within the limits of analytical error.

From the composition of the gas collected in the reservoir (due allowance being made for the small samples withdrawn during the course of the experiment) the amount of sodium cyanide formed or decomposed could be calculated. This was usually the same, within the limits of analytical error, as the amount found by direct analysis of the product in the boat.

By analysis of the gas pumped off at the end of the experiment a control could be obtained of, and a correction applied for, any shift of the equilibrium during the short time required to cool the boat. The shift (towards sodium carbonate) was often capable of detection, but rarely exceeded 1 per cent.

*Analysis of the Product in the Boat.*—The products of all experiments excepting those in which sodium ferrocyanide was the starting material gave a little sodium hydroxide on lixiviation. This was deducted from the total alkali when considering the relation between sodium carbonate and sodium cyanide. The very small amount of alkali (of the order of 0.1 per cent.) that could not be washed out from the excess of carbon was regarded as sodium hydroxide, which was known to be adsorbed much more tenaciously than either sodium carbonate or sodium cyanide. It was occasionally estimated by washing out the iron with mineral acids and burning off the carbon.

*General.*—At temperatures close to  $900^\circ$ , it is an easy matter to obtain fairly consistent results by the procedure outlined above, but at lower and higher temperatures special difficulties enter.

At 850°, the reaction is rather slow, so that it is difficult to bring experiments to completion. Increasing the proportion of catalyst is open to the objection that this increases the quantity of sodium hydroxide found in the product. The plan which was adopted, therefore, was to approach the true equilibrium first from the sodium carbonate side to within about 2 per cent., and then from the sodium cyanide side to about the same degree of approximation. The mean of the two results was taken as the true equilibrium.

At 950°, the main difficulty arose in connexion with the volatility of sodium cyanide, appreciable quantities of which escaped from the boat if the reaction was allowed time for completion. To obviate this, a series of several incomplete reactions, starting first of all with sodium carbonate and carbon, were conducted by passing the gaseous mixture for different lengths of time, all other conditions being identical. A second series was then carried out starting with sodium cyanide. The results of each set, when plotted against the volume of the gas passed, gave two curves approaching a common asymptote, the position of which indicated the true equilibrium.

The values of  $x$  which have been used in calculating the constants of the equilibrium may therefore be classified as individual, mean, and asymptotic. The following table gives some examples of each.

Expt. No.	Temp. (T-273)	Starting point.	100x, (individual).	100p, (mean)	$\log_{10} \left[ \frac{x^2(1-p)^2}{1-x^2} \right]$	23.91-31180/T	$\Delta$	100x (calc.)	$\Delta'$
4	906°	NaCN	0.0	2.3	—	3.45	—	0.0	-2.3
9	914	Na <sub>2</sub> CO <sub>3</sub> +4C	66.1	24.3	3.66	3.63	-0.03	23.9	-0.4
10	909	NaCN	67.8	20.7	3.43	3.52	+0.09	22.8	+2.1
11	917	"	43.0	9.0	—	3.70	—	10.2	+1.2
13	914	"	90.8	86.0	3.66	3.63	-0.03	84.0	-2.0
53	900	Na <sub>2</sub> CO <sub>3</sub> +4C	100.0	98.0	—	3.32	—	100.0	+2.0
Set No.			(mean)						
44	851	Both	82.3	13.6	4.16	4.17	+0.01	13.8	+0.2
46	851	"	60.8	4.2	—	4.17	—	5.3	+1.1
Set No.			(asymptotic)						
29	954	Both	63.8	45.0	2.44	2.51	+0.07	47.0	+2.0
34	950	"	35.8	18.0	2.46	2.42	-0.04	17.2	-0.8
48	900	"	63.8	21.0	3.39	3.32	-0.07	19.8	-1.2

The last three columns of the table exhibit the experimental error. Near the limits of the system no reliance can be placed on values of  $K$  calculated from formula (ii), and therefore the comparison of  $\log_{10} K'$  with 23.91-31180/T is not attempted for values of 100x which are less than 10 or greater than 90. In other cases (10 < 100x < 90), the average error in  $\log_{10} K'$  is  $\pm 0.05$  (8th column). The 9th column contains the values of 100x calculated by formula (iii), whilst the 10th column shows the differences between these and observed values. The average experimental



error amounts to about  $\pm 1.5$  per cent. in the determination of  $\alpha$ . This is equivalent to an average error of  $3^\circ$  in the temperature and is probably due to more than one cause, since the average error in the measurement of temperature is believed to be about  $1^\circ$ . The further reduction of the results has already been summarised on pp. 2280, 2281.

During the course of this work the authors had the advantage of much valuable criticism and advice from Mr. H. N. Beilby and Dr. T. Ewan of the Cassel Cyanide Company, in whose laboratories the experiments were carried out.

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## CCLXXVI.—*The Specific Heats of Gases with Special Reference to Hydrogen.*

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It is well known that observed values of the molecular heats of gases cannot be accounted for on the theory of equipartition excepting in the case of monatomic gases for which  $C_v$  equals  $(3/2)R = 2.977$ , corresponding with three degrees of translational freedom. For a diatomic gas equipartition between three degrees of freedom of translation, two of rotation, and one of vibration, together with the potential energy of vibration gives  $C_v = (7/2)R = 6.947$ , although, actually,  $C_v$  is much less than this and varies considerably with temperature.

Bjerrum suggested (*Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) that energy of vibration should be treated from the point of view of the quantum theory, and on this basis gave the formula  $C_v = \frac{5}{2}R + RF(\nu_1)$  for a diatomic gas,  $F$  being a function, tending towards zero at  $0^\circ$  Abs. and towards unity at high temperatures, which Bjerrum identified with Nernst and Lindemann's expression; and  $\nu_1$  being the frequency.

Bjerrum's theory contains three defects:

(i) He tested his formula with reference to high-temperature measurements only. Since at low temperatures it tends to the limit  $C_v = \frac{5}{2}R = 4.962$ , there is serious lack of agreement with Eucken's values for hydrogen, which fall below 3.0 at low temperatures (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 141).

(ii) Rotational quanta are not considered. However, Krüger has shown (*Ann. Physik*, 1916, [iv], **50**, 346; **51**, 450) that Eucken's results on the specific heat of hydrogen at low temperatures can be represented fairly well, although not exactly, by a Planck-Einstein function of a characteristic precession frequency calculated on the basis of Bohr's atom-model. Krüger, however, does not examine the results to which his theory leads at high temperatures, and, apparently, is not aware of the large difference which the introduction of his term makes to Bjerrum's calculation.\*

(iii) Since Bjerrum leaves the frequency ( $\nu_1$ ) undetermined, one is at liberty to choose the figure which gives the best agreement with observed values, and there is thus a large chance of obtaining satisfactory concordance by accident.†

It will be shown below that the agreement obtained by Bjerrum in the case of hydrogen by the use of an arbitrary frequency is lost when allowance is made for precessional quanta, and that by the use of a vibration frequency having theoretical foundation it is possible to obtain a complete account of the variation of the specific heat of hydrogen over the extreme range of temperature ( $-238^\circ$  to  $2300^\circ$ ) within which measurements have been made. Hydrogen is the only gas for which sufficient data are available at the present time for a satisfactory quantitative test, but the specific heats of other di- and tri-atomic gases tend towards the correct limits, so that there can be no doubt that the principle involved is of general applicability.

We were led to study this subject by certain considerations arising from some measurements made recently by one of us (E. H. U.) of the specific heats of gaseous hydrogen cyanide (this vol., p. 1604), which was found to exhibit "abnormal" behaviour. In the development of the theoretical basis of those experiments, the point arose as to what constitutes "normal" behaviour, and, in order not to overburden the discussion, a general treatment of this subject was promised in a footnote (*ibid.*, p. 1605). It is hoped that the following details relating to hydrogen, and some brief notes on other gases may suffice.

The symbol  $f$  will be used as an abbreviation for the Planck-Einstein function,  $F$  for the Nernst-Lindemann function, and  $\bar{f}$  and  $\bar{F}$  for their average values, defined thus:

\* Bjerrum rejects the idea of a characteristic rotational quantum (*Nernst Festschrift*, 1912, pp. 95—96, footnote).

† Bjerrum evidently realises the seriousness of this defect, as he endeavours (*loc. cit.*) to ascertain if the frequencies chosen can be justified by reference to absorption spectra; however, none of the elementary gases exhibits bands in the positions required, a fact which is discussed in some detail by Sommerfeld ("Atombau und Spektrallinien," 1921, *Mathematische Zusätze*, Nr. 20)

$$f(\nu) = e^{\frac{\beta\nu}{T}} \left\{ \frac{\beta\nu}{T} \right\}^2 / \left\{ e^{\frac{\beta\nu}{T}} - 1 \right\}^3. \quad \bar{f}(\nu) = \frac{1}{T} \int_0^T f(\nu) dT.$$

$$F(\nu) = \frac{1}{2} \{f(\nu) + f(\nu/2)\}. \quad \bar{F}(\nu) = \frac{1}{T} \int_0^T F(\nu) dT.$$

In order to express his results on the specific heats of hydrogen at low temperatures, Eucken used the formula  $C_v = \frac{3}{2}R + Rf(\nu)$ . Here the term  $\frac{3}{2}R$  represents the specific heat due to translation, and the term  $Rf(\nu)$  that due to rotation; vibrations are not considered. As a matter of fact, owing to their larger quantum, the effect of vibrations is negligible within the temperature range covered by Eucken's experiments, although it becomes important at higher temperatures. The complete formula is to be obtained, therefore, by adding to Eucken's formula a term for the specific heat due to vibration, and it is necessary, first of all, to examine the applicability of Eucken's formula at low temperatures in order that any inaccuracies may not be repeated in the complete formula.

To employ Eucken's formula, Krüger (*loc. cit.*) gives  $\nu = 10.06 \times 10^{12}$ , which is calculated from Bohr's constants for the hydrogen molecule (*Phil. Mag.*, 1913, [vi], 26, 487). The agreement, however, is not good, the part of the observed specific heat which should correspond with  $Rf(\nu)$  being uniformly about 13 per cent. too high. Even if the best empirical value,  $\nu_0 = 9.3 \times 10^{12}$  (Nernst, *Verh. deut. physikal. Ges.*, 1916, 18, 83), be used, the improvement is numerically slight, and is of doubtful value, since now the calculated and experimental curves intersect. If, however, we use the theoretical value of  $\nu$  (that is, Krüger's value) and write  $C_v = \frac{3}{2}R + 1.13 Rf(\nu)$ , the concordance is excellent, as the following table shows:

$T_{\text{Abs.}}$	$C_v$ (obs.).	$\frac{3}{2}R + Rf(\nu)$ .	$\Delta$ .	$\frac{3}{2}R + 1.13 Rf(\nu)$ .	$\Delta$ .
40°	2.98	2.98	0.00	2.98	0.00
50	3.01	2.98	+0.03	2.99	+0.02
60	2.99	3.01	-0.02	3.02	-0.03
70	3.10	3.07	+0.03	3.09	+0.01
80	3.14	3.15	-0.01	3.17	-0.03
90	3.26	3.24	+0.02	3.28	-0.02
100	3.42	3.35	+0.07	3.42	0.00
110	3.62	3.47	+0.15	3.54	+0.08
196.5	4.39	4.20	+0.19	4.37	+0.02
273.1	4.75 *	4.52	+0.23	4.74	+0.01
295	4.80 †	4.59	+0.21	4.82	-0.02
		Total	+0.00	Total	+0.04

\* Nernst (*Z. Elektrochem.*, 1911, 17, 272).

† From the literature (average).

The precession theory is manifestly only a first approximation at the present time, and the physical significance of the part  $0.13 Rf(\nu)$

of the specific heat is not clear, although it may be due to some kind of potential energy associated with precessional motion.\*

Having obtained a formula which correctly expresses observed values for temperatures below that at which the effect of vibration begins to be appreciable, we may proceed to calculate the frequency of vibration from numerical data relating to the Bohr model. In conformity with Bohr's view, we must suppose that the stability of the molecule as a whole is determined by the restrictions of the quantum hypothesis, and that any one of the component charges will vibrate only when it acquires one or more quanta from the circumambient radiation.† Further, since displacements of the electrons give rise to frequencies about 1000 times too great appreciably to affect specific heats at attainable temperatures, and since nuclear displacements perpendicular to the axis of the orbit result in motion of the kind considered by Krüger, we have only to consider displacements along the axis. If such a displacement increases the distance,  $b$ , from the centre of the orbit to  $b + db$ , the restoring force will be

$$\frac{2e_0^2(b + db)}{3b^2 + (b + db)^2} - \frac{e_0^2}{(2b + db)^2} = \frac{e_0^2}{4b^2} \cdot \left\{ \left(1 + \frac{db}{b}\right) - \left(1 - \frac{db}{b}\right) \right\} = \frac{5}{16} \cdot \frac{e_0^2 db}{b^3},$$

since the radius of the orbit is  $\sqrt{3}b$ . Hence the frequency is given by

$$\nu' = \frac{\sqrt{5}}{8\pi} \cdot \frac{e_0}{mb^2} = 1.84 \times 10^{14} \text{ vibrations per sec.}$$

The numerical result is obtained by inserting Millikan's values,  $m = 1.662 \times 10^{-24}$  gram, and  $e_0 = 4.775 \times 10^{-10}$  e.s.u., and Bohr's value,  $b = 0.3175 \times 10^{-8}$  cm. Using the experimental data tabulated below and the complete specific heat formulae (i and ii), we find  $\nu' = 1.85 \times 10^{14}$  vibrations per sec. as the average of a number of fairly concordant results.‡

\* McDougal (*J. Amer. Chem. Soc.*, 1921, **43**, 23) has examined the consequences of assuming one degree of freedom due to rotation about the axis joining the nuclei. The logical extension of this idea, however, appears to involve the assumption, for which there is no experimental support, of degrees of rotational freedom for monatomic gases. Moreover the agreement with experiment obtained by McDougal in the case of hydrogen does not appear to us sufficiently exact to warrant the introduction of such a revolutionary supposition.

† In contradistinction to the suppositions made by Bohr (*Phil. Mag.*, 1913, [vi] **26**, 866) in considering the distortions of his systems, the assumed motions of which appear to involve the simultaneous reception of each quantum by all the component charges.

‡ The value of  $\beta = h/k$ , where  $h$  is Planck's constant and  $k$  the gas constant for one molecule, is taken as  $4.773 \times 10^{-11}$  from Millikan's data.

It will be noted that the theoretical value of  $\nu'$  differs considerably from the value,  $\nu_1 = 1.5 \times 10^{14}$ , used by Bjerrum in the formula  $C_v = \frac{5}{2}R + RF(\nu_1)$ . The concordance of this formula with observed values is evidently due to the arbitrary choice of  $\nu_1$ , for it no longer exists when the term  $\frac{5}{2}R$  is replaced by a function, such as  $\frac{5}{2}R + 1.13 Rf(\nu)$ , which is known to fit the data for temperatures at which  $RF(\nu_1)$  is negligibly small.

The following are the complete formulæ for the real and average specific heats of hydrogen:

$$C_v = R[1.50 + 1.13f(10.06 \times 10^{12}) + F(1.84 \times 10^{14})] \quad . \quad . \quad . \quad (i)$$

$$\bar{C}_v(0^\circ - T^\circ) = R[1.50 + 1.13f(10.06 \times 10^{12}) + \bar{F}(1.84 \times 10^{14})] \quad . \quad (ii)$$

It is claimed that their theoretical basis is self-consistent, and that they express observed values over a large range of temperature with an accuracy equal to that of the measurements:

Real specific heat.				Average specific heat.			
		$C_v$	$C_v$			$\bar{C}_v$	$\bar{C}_v$
$T$ .	$T-273$ .	(Obs.).*	(Calc.).	$T$ .	$T-273$ .	(Obs.).*	(Calc.).
273	0	4.75	4.74	1690	1413	5.34	5.34
373	100	4.78	4.85	1777	1504	5.38	5.39
573	300	5.02	5.05	1865	1592	5.42	5.44
773	500	5.20	5.25	2074	1701	5.47	5.49
1073	800	—	5.49	2108	1835	5.52	5.55
1473	1200	5.8 †	5.77	2290	2017	5.61	5.62
2273	2000	6.5 †	6.25	2391	2118	5.65	5.64
3273	3000	—	6.64	2523	2250	5.71	5.67

\* Nernst (*loc. cit.*).

† Approximate only.

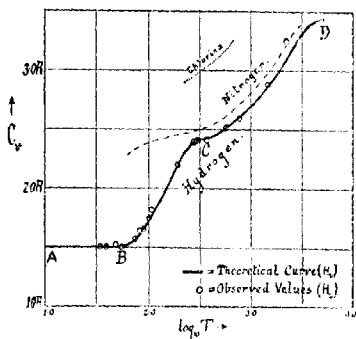
\* Pier (*Z. Elektrochem.*, 1909, 15, 536).

In general, therefore, the specific heat curve of a diatomic gas must consist of three main sections, as may be seen from the diagram, in which the full line represents  $C_v$  for hydrogen plotted against  $\log_{10} T$ .\* At low temperatures, the value,  $\frac{5}{2}R$ , is due to translation only (*AB*); at intermediate temperatures, the rotation quantum becomes appreciable and causes  $C_v$  to rise (*BC*) to about  $\frac{7}{2}R$ , at which point the vibration quantum takes effect and brings about a further rise as shown (*CD*). From a study of such curves for other gases, much can be learnt as to their molecular condition. Thus the high-temperature branch of the curve for nitrogen † (broken line) lies close to the curve for hydrogen, and hence the

\* This is done for convenience in showing very low and very high temperatures on the same diagram.

† Plotted from Scheel and Heuse's measurements at low temperatures (*Ann. Physik*, 1913, 40, 473), and from Pier's data (*loc. cit.*), which show that at high temperatures  $C_v$  for nitrogen is uniformly 0.20 times greater than  $C_v$  for hydrogen at the same temperature.

vibration quanta for these two gases must have similar magnitudes (not so the rotation quanta). Since the motion is simple harmonic (p. 2289), it follows that the force resisting the separation of the nuclei in nitrogen must be nearly fourteen times as great as in hydrogen, and one would expect dissociation to be appreciable only at extremely high temperatures. Similar considerations apply to oxygen and carbon monoxide. In the case of the halogens, on the other hand, their tendency to dissociate at only moderately high temperatures points unmistakably to a small restoring force,



and hence, a small vibration quantum. It is known from Strecker's measurements \* (*Wied. Annalen*, 1881, **13**, 20) of the specific heat ratio ( $\gamma$ ) that the halogens possess unusually high specific heats at the ordinary temperature. The portion of the specific heat curve for chlorine plotted from Strecker's data appears to point to a frequency of about  $3 \times 10^{13}$ , that is, only one-sixth of the frequency of hydrogen, in agreement with the general indications derived from chemical character.

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\* These have been corrected for deviations from the gas laws by means of the formulæ given by Nernst ("Theoretische Chemie," 7. Aufl., s. 245) and the critical constants,  $p_c = 84$  atm. and  $T_c = 419^\circ$  Abs. The values are as follow:

Observed by Strecker.			Corrected.		
$T - 273^\circ$	$p$ (atm.).	$\gamma$ (uncorr.).	$C_p/C_v$	$C_p - C_v$	$C_p$
19	0.61	1.324	1.346	2.057	8.00
100	0.84	1.326	1.339	2.033	8.03
226	0.75	1.321	1.325	2.003	8.16
343	0.50	1.311	1.312	1.991	8.37

CCLXXVII.—*The Constitution of the Terpene Present in the Essential Oil from Andropogon Jwarancusa, Jones.*

By JOHN LIONEL SIMONSEN.

In a recent communication (T., 1921, 119, 1644), mention was made of the fact that, in addition to *d*-piperitone, the essential oil from *Andropogon Jwarancusa*, Jones, contained a small quantity of what appeared to be a new terpene of the formula  $C_{10}H_{18}$ . This hydrocarbon, which did not yield any crystalline derivatives, seemed from its behaviour with bromine and the halogen acids to be bicyclic, and in view of the interest attached to such substances a considerable quantity of the terpene has been purified and investigated in some detail.

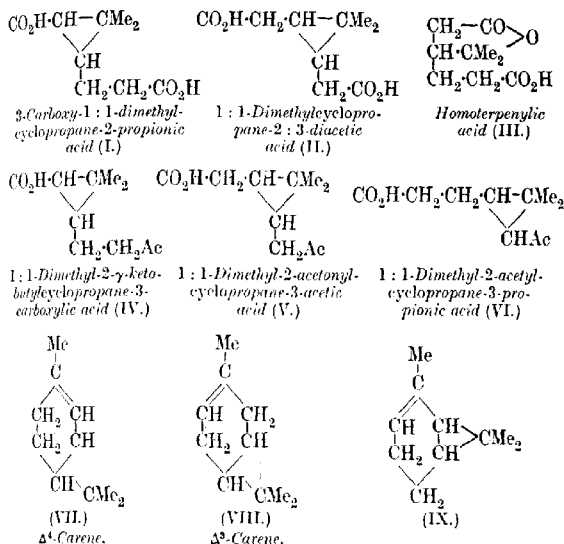
When the hydrocarbon was oxidised with potassium permanganate under the conditions described in the experimental part of this paper (see p. 2295), a saturated liquid *keto*-acid was obtained which, from the analysis of its *ethyl* ester, *semicarbazone* (m. p. 182–183°), and *oxime* (m. p. 124–125°), had the formula  $C_{10}H_{18}O_3$ , and therefore was isomeric with pinonic acid. Although the terpene boiled nearly ten degrees higher than  $\alpha$ -pinene, it was thought desirable, in view of the well-known difficulty of obtaining *d*-pinonic acid crystalline, to compare the derivatives of *d*-pinonic acid directly with those of the new *keto*-acid. A careful comparison of the semicarbazone of *d*-pinonic acid (m. p. 207°) and the oxime (m. p. 127°) with the corresponding derivatives of the *keto*-acid showed at once that they were not identical, and this was confirmed by a comparison of the *semicarbazones* of the *ethyl* esters, that of *ethyl d*-pinonate melting at 152–154°, whereas the semicarbazone of the *ethyl* ester of the new *keto*-acid melted at 119–120°.

Like pinonic acid, the *keto*-acid contained a  $CH_3CO\cdot$  group, since on treatment with sodium hypobromite solution it was converted quantitatively into a saturated, dextrorotatory *dibasic* acid ( $C_9H_{14}O_4$ ) which melted at 104–105° and which was shown by direct comparison not to be identical with *cis*-pinic acid. Further, on treatment with a solution of hydrogen bromide at 100°, it was converted into a lactonic acid ( $C_9H_{14}O_4$ ) which melted at 98–100° and was identified as homoterpenylic acid (III) by direct comparison with a specimen of this acid prepared synthetically (Simonsen, T., 1907, 91, 184).

It has already been shown by Baeyer (*Ber.*, 1896, 29, 3) that pinic acid is not acted upon by hydrogen bromide at 100°, and

the remarkable stability of the "picean" ring has already been discussed by Perkin and Simonsen (T., 1909, **95**, 1166). There can therefore be little doubt that the dibasic acid  $C_9H_{14}O_4$ , which on treatment with hydrogen bromide yielded homoterpenylic acid, must contain a cyclopropane ring.

If this assumption be accepted, the acid can only be represented by formula I or II, whilst the keto-acid would be represented by formula IV, V, or VI.



Keto-acids having the formulæ IV, V, and VI would be derived from hydrocarbons of the formulæ represented by VII, VIII, and IX.

In a paper published some time ago (T., 1920, **117**, 570 \*), the author described a new hydrocarbon which was obtained from the oleo-resin of *Pinus longifolia*. From the fact that this hydrocarbon yielded with hydrogen chloride a mixture of sylvestrene and dipentene dihydrochlorides and on oxidation with potassium permanganate, amongst other products, caronic acid, it was concluded that it must be either  $d$ - $\Delta^3$  or  $\Delta^4$ -carene (VIII or VII). Further, since the molecular refraction was normal ( $[R_L]_D = 44.22$ ;

\* In this paper (p. 574), the decomposition point of carene nitrosate should be  $147.5^\circ$  and not  $141.5^\circ$ . The analysis should read:  $C_{10}H_{16}O, N_2$  requires  $N = 12.3$  per cent.



calc., 44.19), it was considered that in all probability it was  $d\text{-}\Delta^3$ -carene (VIII). The possibility therefore arose that the new hydrocarbon was  $d\text{-}\Delta^4$ -carene (VII).

In view of these results it became desirable to reinvestigate the action of the halogen acids on the terpene, since if it were  $\Delta^4$ -carene it should under suitable conditions yield a mixture of sylvestrene and dipentene derivatives. It had been previously observed (*loc. cit.*, p. 1649) that whereas with hydrogen bromide in acetic acid solution a dihydrobromide resulted, with hydrogen chloride in ethereal solution a monohydrochloride was formed. It has now been found (see p. 2298) that on treatment with hydrogen chloride in acetic acid solution a solid dihydrochloride melting at  $48\text{--}50^\circ$  is formed which has been identified as dipentene dihydrochloride. The bulk of the hydrochloride obtained was, however, an oil and the hydrocarbon regenerated therefrom was found to give an intense sylvestrene reaction with sulphuric acid in acetic anhydride solution. Unfortunately, it has not proved possible to prepare any solid derivatives of this hydrocarbon, but since no other hydrocarbon is known to yield the sylvestrene reaction, the author is of opinion that sylvestrene dihydrochloride was present in the liquid hydrochlorides, although undoubtedly dipentene dihydrochloride formed the main product of the reaction.

The formation of dipentene and sylvestrene dihydrochlorides would appear to prove definitely that the hydrocarbon under investigation must be either  $d\text{-}\Delta^3$ - or  $\Delta^4$ -carene and cannot possess formula IX.

As was mentioned above, owing to its normal molecular refraction it was concluded that the terpene from *P. longifolia* was  $d\text{-}\Delta^3$ -carene and support is lent to this view by the fact that the terpene now under consideration has a very high molecular refraction (Found, in two distinct samples,  $[R_L]_D = 44.69, 44.58$ ). The exaltation is therefore considerable (0.5 and 0.39), although somewhat lower than that observed for sabinene (0.78) (Auwers, Roth, and Eisenlohr, *Annalen*, 1910, 373, 268).

There would appear to be little doubt, therefore, that the hydrocarbon is  $d\text{-}\Delta^4$ -carene (VII), the keto-acid would then be  $d\text{-}1:1\text{-dimethyl-2-}\gamma\text{-ketobutylcyclopropane-3-carboxylic acid}$  (IV), and the dibasic acid  $d\text{-}3\text{-carboxy-1:1-dimethylcyclopropane-2-propionic acid}$  (I).

The occurrence in nature of the two hydrocarbons  $d\text{-}\Delta^3$ - and  $\Delta^4$ -carene would appear to be a matter of some importance and would seem to indicate that we may expect to encounter other derivatives of carane.  $d\text{-}\Delta^4$ -Carene differs considerably in its properties from  $d\text{-}\Delta^3$ -carene; besides having a somewhat lower

boiling point ( $\Delta^4$ , 165.5—167°/707 mm.,  $\Delta^3$ , 168—169°/705 mm.), it is very much less readily oxidised in the air and it does not possess the pungent smell so characteristic of *d*- $\Delta^3$ -carene. It has not so far proved possible to isolate a keto-acid from the oxidation products of *d*- $\Delta^3$ -carene, but further experiments in this direction are in hand and some progress has been made in the difficult problem of synthesising  $\Delta^4$ -carene.

#### EXPERIMENTAL.

The greater part of the terpene used in the experiments detailed below was obtained by the distillation in steam of a quantity of *A. Juarancusa*, Jones, grown in Sind.\* The terpene was found to distil very constantly at 165.5—167°/707 mm. and had the following constants:  $d_{20}^{20}$  0.8552;  $n_D^{20}$  1.474;  $[\alpha]_D^{20}$  + 62.2°;  $[\rho]_D^{20}$  44.69, which except as regards rotatory power agree fairly well with those previously found (*loc. cit.*, p. 1649).

#### Oxidation of *d*- $\Delta^4$ -Carene. *d*-1:1-Dimethyl-2- $\gamma$ -ketobutyl-cyclopropane-3-carboxylic Acid (IV).

As the result of a large number of comparative experiments the following method was found to be the most satisfactory for the oxidation of *d*- $\Delta^4$ -carene. The hydrocarbon (20 c.c.) was dissolved in pure dry acetone (200 c.c.) and to the mixture, which was kept well cooled in an ice-bath, finely divided and sieved potassium permanganate (48 grams) was gradually added. Oxidation proceeded only very slowly and the addition of the permanganate took approximately sixteen hours. When the oxidation was complete, the manganese dioxide was separated, well washed with acetone,† mixed with water, and distilled in steam to remove any adherent acetone and unchanged hydrocarbon. The aqueous solution was filtered and the residual manganese dioxide repeatedly extracted with boiling water until the extract was quite colourless. The manganese dioxide was found to retain the salts of the oxidation acid most tenaciously and as a rule at least six extractions with boiling water were necessary. The alkaline filtrate, which was deep brown in colour, was concentrated to a small bulk in a current of carbon dioxide and acidified, when a viscid, brown oil separated.

\* The oil obtained from *A. Juarancusa*, Jones, grown in Sind, was found to differ very markedly from the oil isolated from the same grass grown in the Hazara District. A detailed account of the composition of the Sind oil will shortly be published in the Indian Forest Records.

† On evaporation, the acetone solution, in addition to unchanged terpene, yielded a small quantity of a viscid oil which distilled at about 185°/67 mm. The oil showed no tendency to crystallise and gave a liquid urethane. It was not further examined.

This was taken up with ether, the ether dried, and evaporated (yield 8 grams). Since the oxidation product, which smelt strongly of acetic acid, showed no tendency to crystallise even on long keeping, it was mixed with excess of semicarbazide acetate solution, when, on warming, a copious precipitate of the semicarbazone separated. This was collected, triturated with ether,\* which removed a small quantity of a resinous brown impurity, and dried on porous porcelain.

The crude *semicarbazone* of the keto-acid melted at 178–180° and was purified by crystallisation from methyl alcohol, from which it separated in glistening rhombohedra melting at 182–183°, and this melting point was not altered by further crystallisation (Found: C = 54.5; H = 7.7.  $C_{11}H_{19}O_3N_3$  requires C = 54.8; H = 7.9 per cent.).

The pure keto-acid was readily obtained by the hydrolysis of the semicarbazone. In one experiment, the semicarbazone (1 part) was heated with dilute sulphuric acid (10 per cent.; 10 parts) on the water-bath for half an hour, when a pale yellow oil had separated on the surface of the sulphuric acid. The acid was taken up with ether, the ether dried and evaporated, when d-1:1-*dimethyl-2-γ-ketobutylcyclopropane-3-carboxylic acid* was obtained as a viscid, pale yellow oil. The acid could not be induced to crystallise even when cooled in solid carbon dioxide. It was found to yield a somewhat sparingly soluble *sodium* salt, which separated from sodium hydroxide solution in prisms. In alkaline solution, it was stable to potassium permanganate, and was not attacked by dilute mineral acids at 100°, although at higher temperatures it appeared to be converted into a lactone.

d-1:1-*Dimethyl-2-γ-ketobutylcyclopropane-3-carboxylic Acid Oxime*.—The acid (1 gram), dissolved in a slight excess of sodium carbonate solution, was heated with hydroxylamine hydrochloride (1 gram) and dilute sodium hydroxide solution (0.6 gram NaOH) on the water-bath for one hour. On cooling and making just acid with hydrochloric acid, the *oxime* separated as a viscid oil, which rapidly solidified. It was purified by crystallisation from dilute methyl alcohol, from which it was obtained in hexagonal prisms melting at 124–125° (Found: C = 60.5; H = 8.8.  $C_{10}H_{13}O_3N$  requires C = 60.3; H = 8.5 per cent.). In methyl alcohol solution (2 per cent.),  $[\alpha]_D^{20}$  was found to be +44.9°.

d-1:1-*Dimethyl-2-γ-ketobutylcyclopropane-3-carboxylic Acid Phenylhydrazone*.—The *phenylhydrazone* of the keto-acid separated

\* In addition to a small quantity of the semicarbazone, the ethereal extract contained a trace of a liquid acid, which was not obtained in sufficient quantity for investigation.

at once as a yellow powder on mixing a dilute acetic acid solution of phenylhydrazine with a solution of the keto-acid in the same solvent. It crystallised from alcohol in long prisms which decomposed at 97—99°. Like the phenylhydrazone of pinonic acid, it was extremely unstable and had completely decomposed on keeping over-night. The *ethyl* ester of the keto-acid,\* prepared in the usual manner with alcohol and sulphuric acid, was obtained as a pleasant-smelling oil which boiled at 133—135°/11 mm. (Found: C = 67.6; H = 9.3.  $C_{12}H_{20}O_3$  requires C = 67.9; H = 9.4 per cent.). The *semicarbazone* of the ethyl ester, prepared in the usual manner in alcoholic solution, was precipitated on the addition of water as an oil which slowly solidified. It crystallised from a mixture of benzene and light petroleum in rosettes of needles which melted at 119—120° (Found: C = 57.8; H = 8.6.  $C_{13}H_{23}O_3N_3$  requires C = 57.9; H = 8.5 per cent.).

*d*-3-Carboxy-1:1-dimethylcyclopropane-2-propionic Acid (I).

In one experiment, the keto-acid (5.5 grams) was dissolved in sodium hydroxide solution (1.5 grams NaOH) and the cooled solution added all at once to a dilute sodium hypobromite solution (275 c.c.; 16.5 grams NaOH, 22 grams  $Br_2$ ). The solution at once became cloudy and after standing for one hour a considerable quantity of bromoform had separated. The excess of hypobromite was removed by sulphur dioxide, the bromoform separated, the solution acidified, saturated with ammonium sulphate, and repeatedly extracted with chloroform. On removing the chloroform, a pale yellow oil (5.5 grams) remained which, on scratching with a glass rod, completely solidified. The dibasic acid, which was somewhat sparingly soluble in cold water, was purified by crystallisation from hot water, from which it separated in minute, irregular plates melting at 104—105°. The acid was found to be readily soluble in all the ordinary organic solvents, and when dissolved in alkaline solution was perfectly stable to potassium permanganate. With copper acetate solution, an aqueous solution of the acid gave an immediate precipitate of a sparingly soluble *copper* salt, which was indistinguishable in appearance from that given by pinic acid (Found: C = 58.3; H = 7.7.  $C_9H_{14}O_4$  requires C = 58.0; H = 7.5 per cent.).

\* For the purposes of comparison, the *semicarbazones* of ethyl *d*- and *l*-pinonate were prepared. These two semicarbazones, which do not appear to have been prepared previously, crystallise from 50 per cent. alcohol in woolly needles melting at 152—154° (Found: in *d*-semicarbazone, C = 57.5; H = 8.2; in *l*-semicarbazone, C = 57.5; H = 8.5. Calc., C = 57.9; H = 8.5 per cent.).

In a 1 per cent. chloroform solution,  $[\alpha]_D^{20}$  was found to be  $+33.5^\circ$ . On titration with a standard solution of potassium hydroxide, 0.197 gram neutralised 13.1 c.c., whereas a dibasic acid,  $C_9H_{14}O_4$ , should have neutralised 13.25 c.c.

*Action of Hydrogen Bromide on d-3-Carboxy-1:1-dimethylcyclopropane-2-propionic Acid. Formation of Homoterpenylic Acid.*

The dibasic acid (0.5 gram), mixed with an aqueous solution of hydrogen bromide (saturated at  $0^\circ$ ; 5 c.c.), was heated for five hours in a sealed tube at  $100^\circ$ . The deep brown solution was evaporated on the water-bath, when a viscid oil was obtained which slowly crystallised. After draining on porous porcelain, it was purified by crystallisation from pure ether, in which it was only sparingly soluble and from which it was obtained in glistening prisms melting at  $98-100^\circ$  (Found: C = 58.3; H = 7.8.  $C_9H_{14}O_4$  requires C = 58.0; H = 7.5 per cent.).

On titration in the cold, 0.1065 gram neutralised 3.6 c.c. of a standard solution of potassium hydroxide (calc., 3.58 c.c.); after boiling the solution with excess of alkali and titrating back, it was found to have neutralised 7.2 c.c.

The lactonic acid was identified as homoterpenylic acid by direct comparison with a synthetic specimen of this acid prepared by the method previously described (Simonsen, *loc. cit.*). A mixture of the two acids melted at  $98-100^\circ$  and they appeared to be identical in every way.

*Action of Hydrogen Chloride on d- $\Delta^4$ -Carene.*

The terpene (10 grams) was dissolved in acetic acid (50 c.c.) and the ice-cold solution saturated with hydrogen chloride, the temperature being kept at  $0^\circ$ . The deep brown solution was kept at  $0^\circ$  for six hours and at the room temperature ( $30^\circ$ ) for forty-eight hours. On pouring into water, a heavy oil separated. This was taken up with ether, the ether thoroughly washed with dilute sodium carbonate solution to remove free acids, dried, and evaporated, and the residual oil distilled under diminished pressure (14 mm.), when practically the whole passed over between  $120-130^\circ$ . On cooling in a freezing mixture, the oil crystallised. On filtering through an ice-cold funnel, a small quantity of a solid hydrochloride was obtained which, after draining on porous porcelain, was crystallised from dilute alcohol, when it was found to melt at  $48-50^\circ$  and was identified as dipentene hydrochloride, since on admixture with an authentic specimen no depression of the melting point was observed.

The liquid hydrochlorides were decomposed by digestion with

sodium acetate in acetic acid solution, when a hydrocarbon was obtained which distilled at 120–140°/200 mm. When dissolved in acetic anhydride and treated with a drop of sulphuric acid, the hydrocarbon gave an intense blue coloration, indicating the presence of sylvestrene. Attempts to prepare solid derivatives of this hydrocarbon were not successful, but the presence of dipentene was confirmed by the preparation of the characteristic tetrabromide.

In conclusion, the author wishes to express his indebtedness to Mr. Gopal Rau for the preparation of a quantity of ethyl  $\beta$ -iodopropionate, and to him and Mr. Ghose for making the analyses.

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[Received, August 30th, 1922.]

### CCLXXVIII.—*Methylation of Xylose.*

By ALBERT CARRUTHERS and EDMUND LANGLEY HIRST.

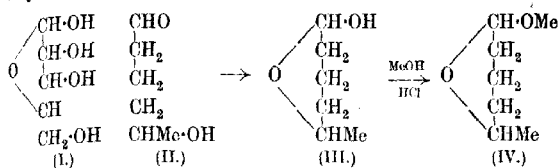
THE importance of investigating in detail the properties of the fully and the partly methylated derivatives of the sugars has long been recognised, not only on account of the interesting constitutional problems presented by these compounds, but also because they serve as standard reference substances which render possible the application of the methylation method to the determination of the structure of the di-, tri-, and poly-saccharides. In view of the wide distribution of glucose and its relationship to cellulose, starch, and glycogen, attention was directed to its study at an early stage in the history of the methylated sugars and in this case investigation of the partly methylated derivatives has been in progress for some considerable time, with the result that the knowledge gained is proving invaluable in the constitutional study of the complex carbohydrates containing glucose residues. Researches now being carried out in this laboratory on the composition of various types of cellulose have revealed the necessity of studying more fully the methylated derivatives of the simple pentoses. Thus it will be shown, in a forthcoming paper by Irvine and Hirst, that the esparto cellulose of the paper manufacturer contains 20 per cent. of xylan, whilst a yield of nearly 19 per cent. of pentosan has been isolated from straw cellulose (Heuser, Braden, and Kirschner, *J. pr. Chem.*, 1921, [ii], **103**, 69). The study of these xylose derivatives by the methylation method will naturally depend on a knowledge of the properties of the fully and the partly methylated xyloses, but up to the present, beyond investigation of the properties of the methyl-pentosides described by Fischer (*Ber.*, 1893, **26**, 2407; 1895, **28**,

1157), the alkylation of pentoses has been restricted to arabinose and rhamnose. In the former case, trimethyl methylarabinoside and the corresponding trimethyl arabinose were prepared and described by Purdie and Rose (T., 1906, 89, 1204), whilst, in addition to the fully methylated rhamnose, Purdie and Young (T., 1906, 89, 1194) obtained a dimethyl derivative and the dimethyl methylrhamnoside corresponding with it. The chemical behaviour of these compounds offers in many ways a very close parallel to that of the methylated hexoses and their methylhexosides, whilst the same regularities regarding optical properties may be applied equally well to both series. Thus the specific rotations of the  $\alpha$ - and  $\beta$ -forms of methylglucoside, methylarabinoside, or methylxyloside are reproduced almost exactly in the values obtained for the  $\alpha$ - and  $\beta$ -forms of the methylated derivatives of these methylhexosides or -pentosides. Examples of this generalisation are collected in the table given below, in which are included figures obtained in the course of the present research for methylated xylose.

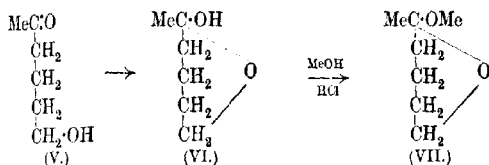
	$[\alpha]_D$		$[\alpha]_D$
$\beta$ -Methylglucoside .....	-33°	Trimethyl $\beta$ -methylxyloside ...	-67°
2 : 3 : 5-Trimethyl $\beta$ -methylglucoside .....	-22.9	$\alpha$ -Methylarabinoside .....	+246
2 : 3 : 6-Trimethyl $\beta$ -methylglucoside .....	-19.9	Trimethyl $\alpha$ -methylarabinoside ...	+251
Tetramethyl $\beta$ -methylglucoside .....	-17	$\alpha$ -Methylglucoside .....	+137
$\beta$ -Methylxyloside .....	-66	Dimethyl $\alpha$ -methylglucoside ...	+143
		Tetramethyl $\alpha$ -methylglucoside ...	+154

Whilst such properties point unmistakably to the possession of some form of lactone ring by all these compounds, it is unfortunately impossible to draw conclusions from them as to whether the linking is of the propylene-, butylene-, or amylenoxide type, or even as to the similarity of the lactone ring structures in different carbohydrates. Thus the optical properties of tetramethyl  $\gamma$ -methylglucoside, the structure of which differs fundamentally from that of the normal forms of tetramethyl methylglucoside, diverge very slightly from those of the  $\beta$ -isomeride. In the light of these arguments and in view of the absence of actual chemical evidence regarding the nature of the linking in the pentose series, the representation of xylose or arabinose by formulæ such as (I) can be regarded merely as a tentative working hypothesis. The need for caution must be further emphasised in view of the recent work of Helferich and Malkomes (*Ber.*, 1922, 55, [B], 702) on the properties of a  $\delta$ -hydroxy-aldehyde (II), which they have shown to be stable in the form of a  $\delta$ -lactone (III), the chemical and physical properties of which exhibit remarkable similarity to those of a normal reducing sugar. Thus, for example, derivatives of a glucoside-like nature may be formed in the usual manner with

acidified methyl alcohol, and this new substance (IV) shows many of the reactions of a normal glucoside, although it possesses an amylene-oxide ring.



Further investigations, now being carried out by Bergmann and Micky (*Ber.*, 1922, **55**, [B], 1390), into the properties of simple hydroxy-ketones such as  $\delta$ -acetyl-*n*-butyl alcohol have shown that these substances form compounds with methyl alcohol resembling methylglucosides with reactivities parallel to those of sugars of the  $\gamma$ -series.



In addition, facts such as the anomalous behaviour of xylose and even of trimethyl xylose in the readiness with which the transformation to furfural may be effected, the failure of xylic acid to form a lactone under ordinary conditions (Allen and Tollens, *Annalen*, 1890, **260**, 307), and the extremely slow condensation of trimethyl xylose with acidified methyl alcohol in the cold, details of which will be found recorded in the experimental part of this paper, are difficult to reconcile with the behaviour of glucose under similar conditions if the two molecules are almost identical in structure. It will be understood, therefore, that although, in depicting the reactions described in the present paper, the butylene-oxide structure is used to formulate xylose and its derivatives, we consider the question as to the exact nature of the linking to be still an open one. Experiments are already in progress by means of which we hope to obtain more definite evidence on this particular point, and in view of the intimate relationship between the hexose and pentose series and the lack of evidence in support of the butylene-oxide structure for the normal hexoses, we hope to extend our studies so as to include the general question of the nature of the oxide ring structure in sugars.



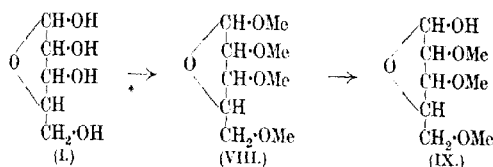
In the study of the methylation of xylose, the considerations advanced above have been kept in view and attention has been particularly directed to those properties on which evidence as to structure might be based and to the possibility of using the methylated compounds as reference substances in the study of the pentosans in a manner similar to that in which the closely analogous penta-, tetra-, and trimethyl-glucoses are being employed in the case of the hexosans. Two series of methylation experiments have been carried out with the view of obtaining the two stereoisomeric forms of trimethyl methylxyloside. Methylation with methyl sulphate according to the method introduced by Haworth for the reducing sugars (T., 1915, 107, 8) followed by treatment with methyl iodide and silver oxide gave the fully methylated, crystalline trimethyl  $\beta$ -methylxyloside (VIII), which was obtained as a wax-like solid, m. p. 46–48°, b. p. 69–72°/0.5 mm. In this case, identification by refractive index measurements is not so convenient as in that of pentamethyl glucose, since preparations of equal purity, but containing differing proportions of the  $\alpha$ - and  $\beta$ -isomerides, and hence superfused to different degrees, gave slightly discordant readings.

With the object of preparing the  $\alpha$ -form of trimethyl methylxyloside, a start was made from the equilibrium mixture of  $\alpha$ - and  $\beta$ -methylxylosides, prepared by treating xylose with acidified methyl alcohol at 160° for twenty hours. Under these conditions, Fischer has shown (*loc. cit.*) that excess of the  $\alpha$ -form is produced and that this may be separated from the  $\beta$ -variety by taking advantage of the different rates of crystallisation of the two isomerides from solution in ethyl acetate. The  $\alpha$ -form, which, in the present series of experiments, could not be separated completely from admixture with a small quantity of the  $\beta$ -form, was methylated by the silver oxide-methyl iodide reaction in the usual manner, using methyl alcohol as solvent during the preliminary stages of the alkylation. The rate of methylation was slow, and before the fully methylated compound was obtained it was found necessary to repeat the treatment no fewer than five times. The final product was a mobile syrup with the following physical constants: b. p. 115–118°/12 mm.,  $n_D$  1.4410 at 25°. A value of  $[\alpha]_D + 86^\circ$  was recorded for the specific rotation in methyl-alcoholic solution. Assuming the applicability to the present case of the generalisation regarding the rotations of methyl pentosides referred to above both  $\alpha$ - and  $\beta$ -forms were present in the specimen in the proportion of 66 per cent. of  $\alpha$ - and 34 per cent. of  $\beta$ -.

The behaviour of both modifications on hydrolysis was distinctly anomalous. When the  $\beta$ -form was hydrolysed under conditions

parallel to those which convert tetramethyl  $\beta$ -methylglucoside quantitatively into tetramethyl glucose, some 50 per cent. only of the calculated quantity of trimethyl xylose was formed. Secondary reactions diminished the yield of sugar, and furfural derivatives were formed in quantity despite the protection to the hydroxyl groups afforded by methylation. Still more unexpected results were forthcoming from the hydrolysis of the mixture containing excess of the  $\alpha$ -form. In this case, milder conditions of hydrolysis were adopted, but notwithstanding these precautions no trace of trimethyl xylose was obtained, a quantity of an exceedingly viscous, levorotatory syrup being isolated, which was acidic in properties.

The trimethyl xylose (IX) which was obtained by hydrolysis of the trimethyl  $\beta$ -methylxyloside crystallised with great readiness and in very characteristic form. The  $\alpha$ -isomeride, after several recrystallisations from ether, showed a maximum melting point of  $87-90^\circ$ , which figure was not altered by further treatment and therefore may be taken as belonging to the pure  $\alpha$ -form of the compound. Mutarotation in aqueous solution was so rapid that the maximum value of  $[\alpha]_D$  for this solvent could not be recorded, but in absolute alcohol the value  $[\alpha]_D + 74^\circ$  was obtained. Catalysis with a trace of ammonia led to very slow mutarotation to a permanent value,  $[\alpha]_D + 21^\circ$ , which was also given by the aqueous solution without a catalyst and by the alcoholic solution on addition of hydrochloric acid, which resulted in very much speedier mutarotation.



For comparison with methylated sugars of the hexose series, the rate of condensation with acidified methyl alcohol in the cold was measured. With 0.25 per cent. acid, no change in rotation was observed after sixty hours at  $15^\circ$ , indicating that the rate of condensation is much slower than in the hexose series. After treatment at  $70^\circ$ , however, a permanent value,  $[\alpha]_D + 50^\circ$ , was recorded, in good agreement with the figure previously found for the equilibrium mixture of  $\alpha$ - and  $\beta$ -trimethyl methylxylosides. This difference in rate of condensation is worthy of note in that it would seem to indicate great stability of structure, whilst the transformation to furfural appears to show the reverse to be the case. The behaviour towards alkaline permanganate resembled that of

normal tetramethyl glucose. Owing to the ease with which the sugar itself could be obtained crystalline, little attention was directed to the attempted formation of derivatives. But in view of the failure of trimethyl arabinose to form an anilide the preparation of the anilide of trimethyl xylose was attempted. This compound, if formed, must be soluble in water and alcohol and must hydrolyse with extreme ease, as all attempts to separate it failed.

Owing to the poor yield of trimethyl xylose which can be obtained from trimethyl methylxyloside, it would appear that for quantitative work greater importance must be attached to the  $\beta$ -form of trimethyl methylxyloside as a reference substance. Its physical constants and the ease and certainty with which it may be obtained crystalline render it of great utility in all cases where it is possible to ensure the formation of the  $\beta$ -form to the exclusion of all but traces of the  $\alpha$ -isomeride.

#### EXPERIMENTAL.

##### *Preparation of Trimethyl Methylxyloside.*

Two separate series of experiments were carried out, in the former of which the object was to isolate finally the  $\beta$ -form of the fully methylated xylose. In this case, methyl sulphate was used as methylating agent and since this is the first occasion on which this reagent has been applied in the pentose series, a description of a typical experiment is given. Xylose (6.6 grams) was dissolved in the minimum quantity of water, and the methylating reagents (50 c.c. of methyl sulphate, and 48 grams of sodium hydroxide dissolved in 93 c.c. of water) were added slowly and simultaneously to the solution. The mixture was vigorously stirred throughout the experiment and the temperature was maintained at 30° until the reducing action on Fehling's solution had disappeared. The remainder of the reagents was added at 70°. Half an hour at the boiling point served to complete the reaction, after which the product was isolated in the usual manner and found to weigh 5.32 grams. Owing to the very volatile nature of the methylated xylose, removal of the solvent requires special care, and in the present case a portion of the material was lost by volatilisation during the elimination of the last traces of the chloroform used in the extraction. The yield is therefore of the same order as that previously found in the hexose series when this method is employed. The resulting mobile syrup crystallised spontaneously, giving long, white needles which melted at 35–40°. Methylation was completed by treatment with silver oxide and methyl iodide in the usual manner, and after two such operations a product was isolated which, on distillation, gave

a colourless, mobile syrup. This crystallised, on cooling, to a wax-like solid which had the following physical constants: b. p. 69—72°/0.5 mm.; m. p. 37—39° (after keeping for one hour).

After keeping for a day on porous tile, the melting point had risen to 45—48°. The superfused solid showed  $n_D^{20}$  1.4316,  $n_D^{25}$  1.4352 [Found: C = 52.46; H = 8.79; OMe = 58.6. Calc. for  $C_5H_6O(OMe)_4$ , C = 52.43; H = 8.74; OMe = 60.1 per cent.]. Chemically this material behaved as a typical glucoside toward Fehling's solution. It was very soluble in water and all the common organic solvents with the exception of light petroleum, in which its solubility was only moderate. As obtained by distillation, the product was a mixture of the  $\alpha$ - and  $\beta$ -forms and from this the pure  $\beta$ -form was isolated by crystallisation from light petroleum, almost the whole of the solvent being removed and the concentrated solution being cooled in ice to effect crystallisation. For the recrystallised specimen the following constants were recorded: m. p. 46—48°;  $n_D^{20}$  1.4316;  $n_D^{25}$  1.4350;  $[\alpha]_D$  - 66.6° in methyl alcohol ( $c = 1.160$ );  $[\alpha]_D$  - 64.0° in ethyl alcohol ( $c = 1.100$ );  $[\alpha]_D$  - 67.0° in water ( $c = 1.114$ ).

In methyl-alcoholic solution the equilibrium value of the specific rotation after treatment with acidified methyl alcohol at 100° for eight hours was  $[\alpha]_D + 49.5^\circ$  ( $c = 1.150$ ).

In the second series of methylation experiments, an attempt was made to obtain the  $\alpha$ -form of trimethyl methylxyloside by methylating  $\alpha$ -methylxyloside, which is obtainable in the manner described by Fischer (*loc. cit.*) from the mixture of  $\alpha$ - and  $\beta$ -methylxylosides resulting by treatment of xylose in sealed tubes with 0.25 per cent. acidified methyl alcohol. Ten grams of xylose were transformed into the methylxylosides, and the  $\beta$ -form was allowed to crystallise. The remaining syrup failed to deposit crystals even after standing for two weeks, and accordingly it was decided to methylate without attempting to separate the last traces of the  $\beta$ -variety. The syrup, weighing 8 grams, was treated in the usual manner with methyl iodide and silver oxide, methyl alcohol being used during the first stages as solvent. Complete methylation required five separate treatments by this method, at the end of which a colourless, mobile syrup (weight 4 grams) was obtained which boiled at 115—118°/12 mm. and which did not crystallise;  $n_D^{20} = 1.4410$ ;  $n_D^{25} = 1.4380$  [Found: C = 52.6; H = 8.66; OMe = 61. Calc. for  $C_5H_6O(OMe)_4$ , C = 52.43; H = 8.74; OMe = 60.1 per cent.].

The value of  $[\alpha]_D$  was + 86° in methyl-alcoholic solution ( $c = 2.534$ ). After digestion with acidified methyl alcohol at 100°, the equilibrium value of the specific rotation was  $[\alpha]_D + 50.4^\circ$  ( $c = 2.301$ ). The

figure previously recorded, starting from the  $\beta$ -form, was  $[\alpha]_D + 49.5^\circ$ .

*Hydrolysis of Trimethyl Methylxyloside.*

The method of hydrolysis adopted was essentially the same as that found very effective for the hydrolysis of tetramethyl methylglucoside. Crystalline trimethyl  $\beta$ -methylxyloside (4.6 grams) was dissolved in 100 c.c. of 8 per cent. aqueous hydrochloric acid, and a small quantity of charcoal added to the solution. The reaction was complete after boiling under reflux for one hour, but the end value of the specific rotation did not correspond with that afterwards found for the equilibrium mixture of the two forms of trimethyl xylose. A considerable amount of a volatile substance was formed which gave an intense red coloration with aniline acetate. This points to the partial destruction of the trimethyl xylose with formation of furfural derivatives. After neutralising with barium carbonate, evaporating to dryness under diminished pressure, and extracting the residues with ether, a pale yellow syrup was obtained which weighed 1.83 grams and crystallised spontaneously. Further extraction of the residues with chloroform gave a small quantity of a syrup which only partly crystallised after several weeks. The total yield was thus slightly less than 50 per cent. of the theoretical value. The crystalline material was moderately soluble in cold ether and could be recrystallised very conveniently from this solvent, in large prisms of characteristic shape and appearance. Analysis proved it to be trimethyl xylose [Found: C = 50.02; H = 8.32; OMe = 48.2. Calc. for  $C_5H_7O_2(OMe)_3$ , C = 50.00; H = 8.33; OMe = 48.4 per cent.]. The substance reduced Fehling's solution and was stable to alkaline potassium permanganate solution. As originally isolated, the substance melted at  $74-77^\circ$ , but after one recrystallisation from ether the m. p. had risen to  $87-90^\circ$ . Further recrystallisation did not raise this figure, which may therefore be taken as corresponding with the pure  $\alpha$ -isomeride. The following observations were made of the specific rotation of the twice recrystallised material:

Solvent.	c.	$[\alpha]_D$ .
Water, initial value .....	1.500	$60^\circ$ ?
"          final .....	1.500	20
Ethyl alcohol, initial .....	0.879	74
"          final .....	0.879	21
Methyl alcohol, initial .....	—	—
"          final .....	1.095	20.1

Owing to the very rapid rate of mutarotation in aqueous solution, the initial value of the specific rotation could not be observed. With ethyl alcohol, a catalyst was required to effect mutarotation, and with a trace of acid the change took place rapidly, the final value

being reached in thirty minutes. With ammonia as catalyst, mutarotation was very slow, requiring several hours for completion.

*Condensation of Trimethyl Xylose with Methyl Alcohol.*—Crystalline trimethyl xylose (0.1095 gram) was dissolved in 10 c.c. of methyl alcohol containing 0.25 per cent. of hydrogen chloride, and the rate of condensation followed polarimetrically. After forty-four hours at room temperature, no change in optical rotation had taken place, and in view of this extreme slowness of reaction at 15° the temperature was raised to 70° and the concentration of acid increased to 0.5 per cent. After eight hours in a sealed tube at this temperature, a permanent value,  $[\alpha]_D + 49.8^\circ$ , was recorded ( $c = 1.182$ ). This agrees well with the observed equilibrium value for  $\alpha$ - and  $\beta$ -trimethyl methylxylosides ( $[\alpha]_D + 49.5^\circ$ ). At this stage the solution no longer reduced Fehling's solution.

*Attempted Formation of an Anilide.*—In accordance with the standard method, the trimethyl xylose was boiled under reflux for five hours with an excess of aniline (5 mols.), dissolved in absolute alcohol. No crystals separated on cooling nor after removal of the greater part of the solvent. The excess of aniline was then removed by distillation in steam, the solution filtered, and evaporated to dryness under diminished pressure. Crystals separated in rosettes of needles and these, after recrystallisation from ether, were recognised as unchanged trimethyl xylose. No trace of an anilide was found at any stage of the experiment.

*Hydrolysis of the Mixture containing Excess of Trimethyl  
 $\alpha$ -Methylxyloside.*

In this case, owing to the known difficulty of hydrolysing  $\alpha$ -glucosides, it was considered advisable to avoid as far as possible conditions conducive to furfural formation, and accordingly sulphuric acid was used in place of hydrochloric acid, and less drastic temperature conditions were employed. The syrup (2.7 grams), obtained as described above, was dissolved in 60 c.c. of 5 per cent. sulphuric acid, and the solution heated for seven hours in a boiling water-bath until the optical rotation,  $[\alpha]_D + 12^\circ$ , ceased to alter in value. The acid was neutralised with baryta, which occasioned a marked colour change, and the resulting neutral solution evaporated to dryness under diminished pressure. The viscous syrup thus isolated did not crystallise on nucleation with a specimen of trimethyl xylose, and it could not be induced to crystallise from ethereal solution. The compound was slightly acid in reaction, gave a considerable proportion of ash on incineration, was appreciably levorotatory ( $[\alpha]_D - 6.4^\circ$ ), and showed OMe = 32.3 per cent. The change of sign in the optical activity on neutralisation, together

with the ash content, would appear to indicate decomposition of the trimethyl xylose with formation of acid products. These changes have not so far been further investigated.

This investigation was carried out in connexion with the Carnegie Trust Research Scheme, and the authors desire to express their indebtedness to the Trustees. They also wish to record their thanks to Principal J. C. Irvine, C.B.E., F.R.S., for the interest he has taken in the work and for his constant criticism and advice.

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CCLXXIX.—*The Velocity of Reaction in Mixed Solvents. Part III. The Influence of Temperature on the Velocity of Saponification of Esters.*

By HAMILTON MCCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and  
RICHARD HARDCASTLE SETTLE.

In Parts I and II of this series (T., 1921, **119**, 970; this vol., p. 243), a study was made of the reaction between the ethyl esters of isobutyric acid, benzoic acid, and mono-substituted benzoic acids and potassium hydroxide in a solvent consisting of alcohol and water. One of the characteristic features of the results obtained was that the curves showing the relation of the velocity constant to the percentage composition of the solvent were very similar and apparently independent of the nature of the ester. It was felt, however, that such a generalisation would not be justified until there was included the study of the reaction between the ethyl ester of a simple aliphatic acid and potassium hydroxide. Measurements have therefore been made with the ethyl esters of *n*-butyric and *n*-heptioic acids.

It was hoped that a comparison between the ethyl esters of the ortho-substituted benzoic acids and the ethyl ester of pivalic (trimethylacetic) acid might lead to an explanation of the abnormal behaviour of the former series of esters; unfortunately, the amount of pivalic acid at our disposal was very limited, and we have not been successful in obtaining a sufficient quantity of the ester in the required state of purity.

It has been pointed out (this vol., p. 252) that the curves showing the relation between the velocity constant and the percentage composition of the solvent are divisible into four linear phases which intersect at such percentage compositions as agree with

simple alcohol-water complexes. These complexes exist, it may be supposed, not only at one definite composition of the solvent, but also at any point of the phase as a dynamic equilibrium between the complex and one of the pair of solvents. An abrupt transition from phase to phase is not suggested and still less that the phases intersect at a point, but rather that there is a gradual change extending over perhaps as much as 2 or 3 per cent. on either side of the theoretical point of intersection. It appears to us impossible to be more precise if we take into consideration the limited number of solvent mixtures that have been examined and, further, the degree of accuracy with which the measurements have been made.

If the assumption, that the peculiar nature of these curves is due to the existence of simple complexes between ethyl alcohol and water, be correct, then confirmatory evidence may be expected from measurements of the physical properties of ethyl alcohol-water mixtures. The evidence available is mainly from measurements of the refractive index, dielectric constant, heat of dilution, freezing point curve, and viscosity. This evidence is by no means consistent when even one physical property is under examination, and if we take into consideration the effect of temperature the inconsistencies are very marked.

A summary is appended of the various complexes which are believed to exist and the measurements from which their existence is deduced. In some cases it has been necessary to plot the values given and calculate the points of discontinuity, so all measurements are referred to alcohol-water mixtures expressed as percentage by weight.

Per cent. alcohol.	Suggested complex.	Measurement.*
80	$5C_2H_5\cdot OH, 3H_2O$ or $3C_2H_5\cdot OH, 2H_2O$	Dielectric constant, viscosity, refractive index.
72.5	$C_2H_5\cdot OH, H_2O$	Dielectric constant.
60	$3C_2H_5\cdot OH, 5H_2O$	Refractive index.
56	$C_2H_5\cdot OH, 2H_2O$	Freezing point, viscosity.
46	$C_2H_5\cdot OH, 3H_2O$	Dielectric constant, density, viscosity.
38 ca.	$C_2H_5\cdot OH, 4(5)H_2O$	Viscosity.
30	$C_2H_5\cdot OH, 6H_2O$	Dielectric constant, heat of dilution, freezing point, viscosity.

\* Dielectric constant (*Z. physikal. Chem.*, 1894, **14**, 296); density (*Pogg. Annalen*, 1869, **138**, 121, 251); refractive index (*Amer. Chem. J.*, 1903, **40**, 470); heat of dilution (*Ann. Chim. Phys.*, 1892, [vi], **27**, 525); freezing point (*T.*, 1894, **65**, 1015); viscosity (*Ber.*, 1886, **19**, 871; *Annalen*, 1862, **123**, 102; *Compt. rend.*, 1903, **137**, 993; *T.*, 1904, **85**, 823; 1909, **95**, 1559).

It will be seen from this summary that confirmatory evidence is obtained for the belief that the discontinuities in our curves are due to the formation of alcohol-water complexes. The existence of the complex  $C_2H_5\cdot OH, 3H_2O$  is very strongly indicated in most



of the physical measurements, but from our determinations of the velocity of saponification of esters at 30° we have found that there is no evidence for the existence of such a complex.

The influence of temperature on these complexes has been studied but little, except in the case of viscosity measurements, and here conflicting results have been obtained. Traube (*Ber.*, 1886, **19**, 871) states that as the temperature is raised from 0° to 20° the maximum moves from 41 to 46 per cent. of alcohol and that a further rise of 10° causes no change in the maximum. Arrhenius (*Z. physikal. Chem.*, 1887, **1**, 285) states, however, that as the temperature is raised from 0° to 55° there is a change in the maximum from 36 to 50 per cent. of alcohol. These results are in strong contrast to those of Dunstan and Thole (*T.*, 1909, **95**, 1559), who find that the maximum is constant over a wide range of temperature but tends to become less pronounced.

In order to obtain information as to the persistence of these complexes at definite points, we have examined the velocity of reaction between the ethyl esters of certain acids and potassium hydroxide in ethyl alcohol-water mixtures over a range of 30°.

The choice of esters which could be examined over a range of 30° was limited by considerations of accuracy and the time necessary for about 60 per cent. of the ester to be saponified. It was considered that the same esters need not be examined both at 15° and 45° in order to give results which are comparable, as it has been found that the nature of the ester is without influence except in the case of the ethyl esters of the ortho-substituted benzoic acids.

#### EXPERIMENTAL.

The determination of the velocity constants was carried out in the manner described in Part I, and the results are shown in Tables I and II.

TABLE I.  
Ethyl *n*-butyrate (b. p. 118°). Temperature 30°.

Per cent. alcohol.	$k_{KOH}$ .	$k_{ester}$ .	Limit $k$ .	$k$ .
95	0.06267	0.03333	0.0715—0.073	0.0725
90	0.06429	"	0.116—0.123	0.118
85	0.03900	0.02222	0.150—0.159	0.153
82.5	0.03756	"	0.185—0.200	0.190
80	0.04170	"	0.21—0.23	0.215
70	0.04442	"	0.24—0.26	0.25
60	0.03909	"	0.32—0.345	0.33
50	0.01585	0.01111	0.51—0.53	0.52
45	0.01653	0.00741	0.60—0.63	0.625
40	0.01142	0.00667	0.72—0.76	0.735
35	0.01642	0.00833	0.85—0.87	0.86
30	0.01053	0.00444	0.95—1.05	1.00
25 *	0.01385	0.00667	1.4—1.6	1.50
20 *	0.00623	0.00347	1.95—2.08	2.05

TABLE II.

Ethyl *n*-heptoate (b. p. 95°/35 mm.). Temperature 30°.

Per cent. alcohol.	$C_{\text{соя.}}$	$C_{\text{ester}}$	Limit $k$ .	$k$ .
95	0.06267	0.03333	0.079—0.083	0.080
90	0.03898	0.02222	0.124—0.134	0.128
85	0.04016	"	0.169—0.182	0.174
82.5	0.04326	"	0.195—0.202	0.200
80	0.04170	"	0.215—0.230	0.225
70	0.04130	"	0.265—0.285	0.27
60	0.05012	"	0.30—0.32	0.31
50	0.01585	0.01111	0.435—0.46	0.45
45	0.01766	0.00833	0.50—0.54	0.51
40	0.01287	0.00667	0.57—0.60	0.59
35 *	0.00536	0.00267	0.79—0.82	0.80
30 *	0.00326	0.00144	1.02—1.11	1.06

The preparation of a standard solution of both these esters in a solvent marked \* was found to be difficult; the volume of solvent required for 0.2 gram of the ester was so large that the distinction between fine suspension and true solution was not always appreciable. The results from two determinations of the value of  $k$  are recorded, but it is felt that these values should be used only as an indication of the direction of the curve. The critical points, determined from a study of the curves and also by mathematical analysis, are shown in Table III:

TABLE III.

Ester.	Critical points (per cent. of alcohol) at 30°.		
Ethyl <i>n</i> -butyrate .....	80.7	59.0	30 ca.
" <i>n</i> -heptoate .....	80.6	60.0	—

These values show that the esters of the simple aliphatic acids give percentage compositions for the critical points which correspond closely with those previously obtained with other esters.

A noticeable feature in the results is that ethyl *n*-heptoate is saponified more rapidly than ethyl *n*-butyrate in a solvent containing more than 60 per cent. of alcohol. The difference in velocity is not large, but it persists in every measurement and is greater than could be accounted for by experimental error. This is a reversal of what might be expected from a consideration of the results obtained by Reicher (*Annalen*, 1885, **228**, 283), who studied the velocity of saponification of the ethyl esters of some of the lower members of the aliphatic acids with sodium hydroxide in aqueous solution and found that  $k$  diminished with increasing length of the carbon chain (Table IVa).

In a solvent containing less than 60 per cent. of alcohol ethyl *n*-butyrate is saponified more rapidly than ethyl *n*-heptoate, and is thus in accord with Reicher's results.

TABLE IVa.

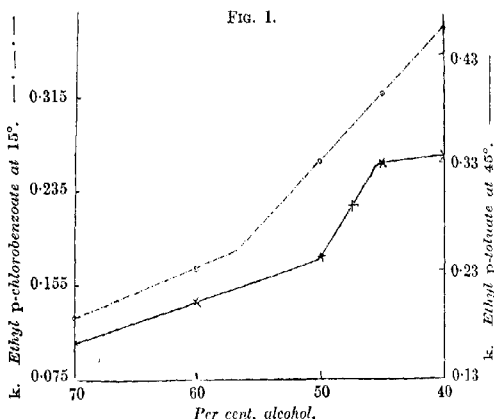
Ester.	$k_{15^\circ}$ .
Ethyl acetate .....	3.22
" propionate .....	2.82
" butyrate .....	1.70
" isobutyrate .....	1.71
" isovalerate .....	0.62
" benzoate .....	0.83

TABLE IVb.

Per cent. alcohol.	$k_{30^\circ}$ . <i>n</i> -Butyrate.	$k_{30^\circ}$ . <i>n</i> -Heptoate.
95	0.0725	0.080
90	0.118	0.123
85	0.153	0.174
82.5	0.190	0.200
80	0.215	0.225
70	0.25	0.27
60	0.33	0.31

*The Influence of Temperature.*

The esters chosen for examination at 15° were ethyl *o*-chlorobenzoate, ethyl *p*-chlorobenzoate, and ethyl *n*-butyrate; and at 45°, ethyl *o*-iodobenzoate, ethyl *p*-toluate, and ethyl isobutyrate.



In each case there is a representative aliphatic and aromatic ester and also an ester of the abnormal ortho-substituted aromatic type.

The measurements at 15° were carried out exactly in the manner described for those at 30°. The thermostat was regulated to  $\pm 0.05^\circ$  by an Ostwald type of regulator or by a regulator admitting ice-cooled water to the thermostat.

The procedure in making the measurements at 45° had to be modified, as it was feared that appreciable changes in the composition of the solvent might occur if the flask were opened some ten or eleven times during the course of the reaction. Therefore the reaction mixture was made up and kept at 15° or slightly below this temperature and 10 c.c. of this mixture were transferred to a 30 c.c. conical flask previously immersed in the thermostat, and the flask was immediately stoppered. The commencement of

the reaction was assumed to be that time at which delivery was made into the flask. The division of the reaction mixture into two portions gave a maximum time of four minutes between mixing and transference to the thermostat. A blank experiment showed that 10 c.c. of the reaction mixture run into the previously warmed flask attained a temperature of  $45^{\circ}$  in thirty seconds after delivery from the pipette. The small flasks were removed from the thermostat, acid was run in to within about 0.5 c.c. of the end-point, and then the titration finished.

The possible errors arising from this method of calculating the commencement of the reaction may influence the actual value of the constant to a very slight extent, but it was found that the constants as determined from ten experimental flasks were in closer agreement with one another than in the measurements at  $30^{\circ}$ , and comparative experiments gave deviations, from a mean value, of about  $\pm 2$  per cent. actual.

The results are shown in the following tables (V--XII) and in the curves :

TABLE V.

Ethyl *n*-butyrate. Temperature  $15^{\circ}$ .

Per cent. alcohol.	$\kappa_{\text{кон.}}$	$\kappa_{\text{center-}}$	Limit $k$ .	$k$ .
90	0.04098	0.02222	0.0276—0.0286	0.0283
85	0.04051	"	0.0388—0.0412	0.040
82.5	0.05180	"	0.0438—0.0460	0.045
80	0.04287	"	0.054—0.060	0.055
70	0.04240	"	0.078—0.081	0.079
60	0.03962	"	0.107—0.114	0.110
50	0.04270	"	0.167—0.176	0.172
45	0.04238	"	0.209—0.220	0.214
40	0.04847	"	0.243—0.250	0.245
35	0.02168	0.01333	0.355—0.375	0.365
32.5	0.02329	0.01044	0.41—0.43	0.415
30	0.02787	0.01333	0.44—0.475	0.465
25	0.02492	0.01111	0.755—0.78	0.77
20	0.02564	"	1.04—1.11	1.06

TABLE VI.

Ethyl *p*-chlorobenzoate. Temperature  $15^{\circ}$ .

Per cent. alcohol.	$\kappa_{\text{кон.}}$	$\kappa_{\text{center-}}$	Limit $k$ .	$k$ .
90	0.06592	0.03333	0.044—0.046	0.045
85	0.06436	"	0.060—0.063	0.0615
82.5	0.06265	"	0.072—0.073	0.0725
80	0.06020	"	0.075—0.077	0.0765
70	0.07036	"	0.096—0.104	0.098
60	0.05890	0.02222	0.119—0.124	0.120
50	0.04719	0.03333	0.162—0.171	0.166
45	0.05045	0.02222	0.189—0.195	0.193
40	0.04163	0.01333	0.216—0.230	0.220
35	0.01681	0.00500	0.30—0.324	0.31
30	0.01764	0.00667	0.41—0.425	0.42

TABLE VII.

Ethyl *o*-chlorobenzoate. Temperature 15°.

Per cent. alcohol.	с <sub>кон.</sub>	c <sub>ester</sub>	Limit k.	k.
90	0.06592	0.03333	0.032—0.033	0.032
85	0.06436	"	0.0385—0.0395	0.039
82.5	0.06265	"	0.0415—0.043	0.042
80	0.05871	"	0.0515—0.054	0.053 } *
	0.06035	"	0.044—0.046	0.045
70	0.05036	"	0.044—0.046	0.0455
60	0.05890	"	0.048—0.0495	0.049
50	0.04719	"	0.064—0.068	0.067
45	0.05045	"	0.081—0.0845	0.0825
40	0.04163	0.02222	0.091—0.0945	0.092
35	0.02241	0.01111	0.131—0.142	0.134
32.5	0.01757	0.00688	0.158—0.170	0.162
30	0.02787	0.01111	0.188—0.195	0.192
25	0.00393	0.00192	0.355—0.380	0.37
20	0.00343	0.00167	0.515—0.540	0.535

\* It will be noticed that two values are given for the constant obtained with a solvent containing 80 per cent. of alcohol. Both results have been confirmed. This peculiar behaviour has been observed also in the case of ethyl *o*-bromobenzoate in the same solvent at 30°.

A consideration of the results given in Tables V—VII, together with the curves, shows that the general character of the curves, for the same esters, is the same as at 30°. At the latter temperature, a phase exists from 40 to 60 per cent. of alcohol, but below 40 per cent. the curve swings slowly up to 35 per cent. and then more steeply to 30 per cent. of alcohol. It is found that at 15° there is between *k* and the composition of the solvent a linear relationship existing between 40 and 30 per cent. of alcohol which has been confirmed by a determination at 32.5 per cent. of alcohol. Thus at 15° the evidence seems to point to the existence of the following complexes:

TABLE VIII.

Ester.	Critical points (per cent. alcohol) at 15°.			
Ethyl <i>n</i> -butyrate .....	80.2	59	39.5	30
" <i>p</i> -chlorobenzoate .....	81.5	58	38.7	
" <i>o</i> -chlorobenzoate .....	80.5	62.5	38.6	30

The values found for the critical points are substantially those found at 30° with the addition of the point at 39 per cent. of alcohol. This composition of the solvent corresponds with a complex  $C_2H_5 \cdot OH \cdot 4H_2O$ , the probable existence of which has been predicted from viscosity measurements.

A consideration of the results given in Tables IX—XI, together with the curves, shows that the general character of the curves is the same for the same esters at 45° as at 30°. A marked dissimilarity occurs, however, in that at 45° there is one phase only between

TABLE IX.  
Ethyl isobutyrate. Temperature 45°.

Per cent. alcohol.	$\kappa_{OH}$ .	$\kappa_{ester}$ .	Limit $k$ .	$k$ .
90	0.04093	0.02222	0.126—0.137	0.134
85	0.04240	"	0.191—0.197	0.195
82.5	0.03971	"	0.212—0.225	0.217
80	0.04093	"	0.246—0.254	0.252
70	0.03380	0.01667	0.306—0.336	0.32
60	0.02467	0.01333	0.36—0.38	0.37
50	0.01437	0.00667	0.62—0.67	0.64
47.5	0.01300	"	0.75—0.77	0.76
45	0.02712	"	0.795—0.85	0.82
40	0.01182	0.00391	0.95—1.07	1.00
35	0.01200	"	1.20—1.34	1.26
30	0.00626	"	1.50—1.63	1.57
25	0.00312	0.00167	2.25—2.36	2.3

TABLE X.  
Ethyl *p*-toluate. Temperature 45°.

Per cent. alcohol.	$\kappa_{OH}$ .	$\kappa_{ester}$ .	Limit $k$ .	$k$ .
90	0.04135	0.02222	0.0815—0.0848	0.083
85	0.04093	"	0.098—0.102	0.100
82.5	0.04629	"	0.107—0.113	0.110
80	0.03986	"	0.127—0.133	0.130
70	0.03986	"	0.164—0.170	0.168
60	0.03518	0.01667	0.192—0.198	0.196
50	0.02635	0.01333	0.234—0.242	0.238
47.5	0.02617	"	0.277—0.295	0.285
45	0.02712	"	0.321—0.330	0.328
40	0.02816	0.01111	0.333—0.342	0.336
35	0.01509	0.00759	0.455—0.480	0.465
30	0.01549	0.00667	0.64—0.68	0.65

TABLE XI.  
Ethyl *o*-iodobenzoate. Temperature 45°.

Per cent. alcohol.	$\kappa_{OH}$ .	$\kappa_{ester}$ .	Limit $k$ .	$k$ .
90	0.03870	0.02222	0.160—0.167	0.163
85	0.03840	"	0.178—0.183	0.180
82.5	0.03369	0.02500	0.181—0.185	0.183
80	0.03220	0.02222	0.185—0.194	0.190
70	0.04412	0.02500	0.220—0.229	0.222
60	0.03318	0.01818	0.246—0.256	0.250
50	0.03542	0.02045	0.265—0.273	0.270
47.5	0.02617	0.01667	0.294—0.301	0.296
45	0.03662	0.02045	0.340—0.350	0.345
40	0.02214	0.00818	0.35—0.37	0.36
35	0.01653	0.00750	0.47—0.485	0.48
30	0.00975	0.00432	0.655—0.685	0.675

50 and 80 per cent. of alcohol and then a marked break occurs between 45 and 50 per cent. of alcohol. This break has been confirmed by a determination in a solvent containing 47.5 per cent. of alcohol.

It would appear from these determinations that at 45° the following complexes may exist :

TABLE XII.

Ester.	Critical points (per cent. alcohol) at 45°.		
Ethyl isobutyrate .....	81.2	47	30 ca.
" <i>p</i> -toluate .....	81.5	45.7	
" <i>o</i> -iodobenzoate .....	81.2	45.7	

The critical point at about 80 per cent. of alcohol is in agreement with the values found at 15° and 30°.

The point of intersection occurring at 59 per cent. of alcohol (62.5 per cent. of alcohol in the case of the ortho-substituted aromatic esters) at 15° and 30° has disappeared at 45°; the two phases which intersected at this point at the lower temperatures did not differ greatly in slope, yet the point of intersection occurred within a range of 2.5 per cent. and persisted for a large number of esters. As a result of the order in which the various measurements were made, a similar change in direction in the curve was expected at 45°, since the values of *k* in 80, 70, and 60 per cent. alcohol were found to lie on a straight line and the values of *k* in 60, 45, and 40 per cent. alcohol were found to form a second straight line. In order that a point of intersection should occur at 60 per cent. of alcohol, it would be necessary that the value of *k* in 50 per cent. alcohol should lie on the second straight line, whereas it was found that, on extrapolation, the first line passed through this value of *k*. This unexpected result was confirmed by check determinations and by a determination of *k* in 47.5 per cent. alcohol; a marked break in the curve has been discovered at 46 per cent. of alcohol.

The complex represented by the composition 46 per cent. alcohol would be  $C_2H_5\cdot OH, 3H_2O$ , a complex for the existence of which exceptionally strong evidence is available. The appearance of this complex has led to a reconsideration of the results at 15° and 30° to see if such a break in the curve has been missed, but it was found that the change in direction at 59 per cent. of alcohol would tend to mask any peculiarities at 46 per cent. of alcohol to such an extent that they would be accounted for as experimental error.

A consideration of the values obtained for the critical points at each of the three temperatures shows that only those points occurring at 80 and 30 per cent. of alcohol persist over the range of 30°, and are equally well marked at the higher as at the lower temperature. The complex represented by the composition 30 per cent. of alcohol must exist over a wide range of temperature, since

its existence is deduced from the freezing-point curve for alcohol and water mixtures, and such a mixture has a freezing point of about  $-20^{\circ}$ .

The critical point at 62.5 per cent. of alcohol is peculiar to the ortho-substituted aromatic esters and is very well defined at  $15^{\circ}$  and  $30^{\circ}$ , but is not apparent at  $45^{\circ}$ , which would seem to indicate that the complex  $2C_2H_5\cdot OH, 3H_2O$  is not capable of existing at a temperature approaching  $45^{\circ}$ .

There are two possible complexes,  $3C_2H_5\cdot OH, 5H_2O$  and  $C_2H_5\cdot OH, 2H_2O$ , which could exist within the compositions 60.5 and 56 per cent. of alcohol, and the slight change of slope in the curve at  $15^{\circ}$  and  $30^{\circ}$  renders a decision very difficult; the results in this work seem to indicate the first possibility, and other physical measurements the second. It is evident, however, that the stability of these complexes is not great, since at  $45^{\circ}$  the curve shows no break or change of direction.

The complex  $C_2H_5\cdot OH, 3H_2O$  is apparent only at  $45^{\circ}$  in these measurements possibly on account of the reasons given previously, but the evidence from other sources leaves little doubt that this complex is stable over a wide range of temperature.

A study of viscosity data shows that a rather indefinite complex of the composition  $C_2H_5\cdot OH, 4(5)H_2O$  exists at  $25^{\circ}$ , and the curves seem to confirm the existence of such a complex at the temperature of  $15^{\circ}$ .

#### Summary.

1. The curve showing the relation between the value of  $k$  and the percentage composition of the solvent is divisible into a series of straight lines.
2. The points of intersection of these straight lines occur at such compositions of the solvent as correspond with simple alcohol-water complexes.
3. Six alcohol-water complexes seem to be indicated by the results, the compositions being  $5C_2H_5\cdot OH, 3H_2O$ ,  $2C_2H_5\cdot OH, 3H_2O$ ,  $3C_2H_5\cdot OH, 5H_2O$ ,  $C_2H_5\cdot OH, 3H_2O$ ,  $C_2H_5\cdot OH, 4H_2O$ , and  $C_2H_5\cdot OH, 6H_2O$ .
4. The complex formed does not depend on the nature of the ester except in the case of the ortho-substituted aromatic esters, where a complex,  $2C_2H_5\cdot OH, 3H_2O$ , appears to be formed in preference to the complex  $3C_2H_5\cdot OH, 5H_2O$ .
5. The stability of a complex appears to be dependent on the temperature, since the complex  $C_2H_5\cdot OH, 4H_2O$  is not observed at  $30^{\circ}$  and the complexes  $3C_2H_5\cdot OH, 5H_2O$  and  $2C_2H_5\cdot OH, 3H_2O$  are not apparent at  $45^{\circ}$ .
6. The temperature coefficient is dependent on the composition



of the solvent, falling steadily as the percentage of water is increased until a minimum value of 2 per 10° is reached.

The authors wish to express their thanks to Mr. A. E. Cashmore for undertaking the measurements with ethyl *o*-iodobenzoate and also for numerous confirmatory measurements, and to the Government Grant Committee of the Royal Society for a grant which has helped to defray the expenses of this work.

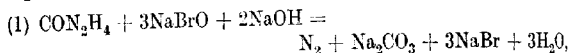
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[Received, August 10th, 1922.]

CCLXXX.—*The Constitution of Carbamides. Part XIV.  
The Decomposition of Urea by Sodium Hypobromite  
in Alkaline Solution, and an Improved Procedure  
for the Estimation of Urea by this Means.*

By EMIL ALPHONSE WERNER.

WHEN urea is decomposed by 'alkaline hypobromite,' under the conditions usually adopted, it is well known that the change represented by the equation



is not quantitatively realised in practice.

A deficiency, roughly of 8 per cent., in the volume of nitrogen evolved was the first failing recognised.

Fenton (T., 1878, **33**, 300; 1879, **35**, 12) and Foster (T., 1879, **35**, 120) showed that this was due to the fixation of a portion of the nitrogen as alkali cyanate during the progress of the reaction. Fauconnier (*Bull. Soc. chim.*, 1880, [iii], **33**, 103) directed attention to the formation of a small amount of nitric acid during this decomposition of urea. Luther (*Z. physiol. Chem.*, 1889, **13**, 500) claims to have shown that from 3 to 4 per cent. of the nitrogen was oxidised to nitric acid when urea was decomposed by an excess of barium hypobromite. From the results recorded in the present paper, it is certain that this amount of nitrogen was not 'fixed' as nitrate when urea was decomposed by sodium hypobromite in alkaline solution.

Whilst Krogh (*Z. physiol. Chem.*, 1913, **84**, 379) noted the presence of carbon monoxide as a product of the reaction, Hurtle (*Biochem. J.*, 1921, **15**, 11) showed that the gas evolved from a 2 per cent. solution of urea, when attacked by 'hypobromite' of the usual

strength, contained on an average 0.7 per cent. of carbon monoxide. Since this approximately compensates for the nitrogen fixed as nitrate, it is obvious that, so far as the estimation of urea is concerned, the formation of alkali cyanate is the chief disturbing effect in the reaction.

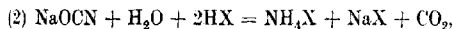
Considering the numerous investigations which this decomposition of urea has called forth during the last forty years, it is curious that no attempt has hitherto been made to determine directly the volume of nitrogen fixed during the reaction as alkali cyanate. The fact that the formation of the latter has not received the full attention it deserves—particularly from continental investigators—is no doubt responsible for this important omission.

It is obvious that, since a cyanate is produced, neither the amount of carbonate formed nor the amount of 'hypobromite' destroyed could give a result in agreement with the requirements of the above equation (1). Dekeuwer and Lescœur (*Compt. rend. Soc. Biol.*, 1919, 82, 445), apparently without considering this point, have confirmed the fact by direct experiments, whilst Brahm (*Chem. Zentr.*, 1919, iv, 442) advocates the rejection of all methods for the estimation of urea which are based on its reaction with 'alkaline hypobromite.'

The author is not prepared to go so far, since the following procedure has been found to give almost theoretical results.

Two operations being necessary, a nitrometer is the most convenient form of apparatus to use.

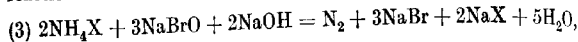
The solution of urea is added in the usual manner to a small excess of 'alkaline hypobromite' contained in the nitrometer. After about twenty minutes the volume of gas evolved, having been carefully recorded, is expelled from the nitrometer. Sulphuric acid (1 in 5 of water) is now added to the residual liquid until the latter, after careful mixing, shows the *permanent* presence of free bromine. The carbon dioxide liberated from the solution by this treatment must not \* be expelled from the apparatus. After fifteen minutes, to allow for hydrolysis of the cyanic acid set free, in accordance with the change



odium hydroxide solution (30 per cent.) is added in excess. Whilst this regenerates 'hypobromite' from the free bromine present, it is nevertheless advisable to add a small quantity of the reagent to the residual solution. After complete absorption of the carbon

\* During the process of adding the acid, and mixing the solution, reactions 2) and (3) take place to a small extent, and hence there is loss of some nitrogen if the gas is expelled.

dioxide, the volume of the gas produced, as a result of the reaction



is added to the volume of nitrogen recorded in the first stage. In the table of results given below, the two stages are referred to as (a) and (b) respectively.

In each case 0.06 gram of urea was used, equal to 22.4 c.c.  $\text{N}_2$  at *N.T.P.*

TABLE I.

Expt.	Urea per cent.	C.c. of gas at <i>N.T.P.</i>		Total.	Percentage of total N. in urea.
		(a)	(b).		
1	1	20.44	1.84	22.28	99.46
2	2	20.48	1.88	22.36	99.82
3	3	20.52	1.82	22.34	99.75
4	6	20.10	2.30	22.40	100.00

Allowing for the presence of a small quantity of carbon monoxide in the gas evolved in stage (a), it is evident from the above results that the amount of nitrogen fixed as nitrate cannot be more than about 1 per cent.

The question arises: Can the formation of cyanate be suppressed? Duggan (*J. Amer. Chem. Soc.*, 1882, **4**, 47) obtained volumes of gas, assumed to be pure nitrogen, varying from 99.02 to 99.91 per cent. of the theoretical, by generating the 'hypobromite' *in situ* with urea. Le Comte (*J. Pharm. Chim.*, 1903, [vi], **17**, 471) claims to have obtained all the nitrogen of urea by a similar procedure.

The following results were obtained when the method proposed by Duggan was completed by the addition of the second stage. In each experiment 0.06 gram of urea was dissolved in 20 per cent. sodium hydroxide solution, after which bromine was added in amount as recommended by Duggan.

TABLE II.

Expt.	Urea per cent.	C.c. of gas at <i>N.T.P.</i>		Total.	Percentage of total N. in urea.
		(a).	(b).		
1	0.5	21.81	0.82	22.63	101.0
2	1.0	21.54	0.89	22.43	100.1
3	2.0	21.63	0.95	22.58	100.8
4	3.0	21.87	0.66	22.53	100.5

Whilst the formation of cyanate is considerably suppressed when the 'hypobromite' is generated in the alkaline solution of urea, the reaction under such condition is extremely violent. All observers agree on the point that excess of alkali promotes the decomposition of urea by hypobromite, and Krogh and Hurley (*loc. cit.*) showed that the volume of carbon monoxide evolved increased with the alkalinity of the reagent.

The excess of gas over the theoretical value for nitrogen in the above experiments was due to this fact.

*The Decomposition of Urea by Alkaline Hypobromite in the Presence of Dextrose.*

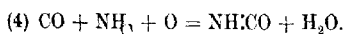
Méhu (*Compt. rend.*, 1879, **89**, 175) claimed that all the nitrogen (<sup>1</sup>) of urea was evolved when the decomposition by 'alkaline hypobromite' was effected in the presence of dextrose. Supported by the fact that the sugar alone does not evolve any gas when mixed with the reagent, Méhu's procedure has been adopted in certain quarters for the estimation of urea, on the assumption that dextrose enhances the evolution of nitrogen. The following results clearly prove that it does nothing of the kind.

Pure dextrose was added to 0.06 gram of urea in 3 c.c. of water, after which an excess of alkaline\* hypobromite was added, the experiments being completed by the addition of the second stage. Theoretical yield of N<sub>2</sub> = 22.4 c.c. at N.T.P.

TABLE III.

Expt.	Urea.	Dextrose.	C.c. of gas at N.T.P.		Total.	Percentage of total N. in urea.
			(a).	(b).		
1	0.06	nil	20.42	1.84	22.26	99.37
2	"	0.06	20.88	1.96	22.84	101.96
3	"	0.12	21.34	1.93	23.27	103.88
4	"	0.18	21.92	1.97	23.89	106.65
5	"	0.24	22.34	1.92	24.26	108.30

It will be seen that whilst the addition of dextrose leads to a proportionate increase in the volume of gas set free in the first stage, its presence has practically no effect on the volume of gas liberated in the second stage. Therefore, since dextrose does not prevent the formation of cyanate, it cannot promote evolution of nitrogen which is fixed from this cause during the primary reaction. The gradual increase in the volumes of gas under (a) was due to carbon monoxide, the presence of which was proved by the usual tests for this gas. Whilst it is true that no carbon monoxide was evolved when alkaline hypobromite was added to dextrose alone, that is, within a reasonable lapse of time, this gas was always generated in appreciable quantity when a salt of ammonia was decomposed by the reagent in the presence of dextrose. This is an interesting point, since more or less cyanic acid is formed, as a result of the reaction



\* Since oxidation of the sugar gives rise to much carbon dioxide, the absorption of this gas was ensured by adding a little extra alkali.

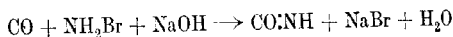
By means of the method adopted for stage (b), the amount of cyanic acid generated in this way was easily determined.

The results given below were obtained by adding an excess of alkaline hypobromite to 0.0535 gram of ammonium chloride, and the stated amounts of dextrose, dissolved in 3 c.c. of water. A control experiment with the ammonium salt alone was made for comparison, since the theoretical yield of nitrogen was not evolved, on account of the fixation of a portion as nitrate. Theoretical yield of  $N_2 = 11.2$  c.c. at *N.T.P.*

TABLE IV.

Expt.	$NH_4Cl$ .	Dextrose.	C.c. of gas at <i>N.T.P.</i>		Total.	Calculated on percentage of nitrogen in $NH_4Cl$ .
			(a).	(b).		
1	0.0535	nil	10.95	no gas	10.95	97.76
2	"	0.03	10.58	0.80	11.38	101.60
3	"	0.06	10.35	1.29	11.64	103.98
4	"	0.09	10.22	1.87	12.09	107.94
5	"	0.12	10.11	2.13	12.24	109.28

When compared with the results given in Table III, it will be seen that in spite of the fact that the gas evolved in stage (a) contained carbon monoxide (except experiment 1), the volume of gas diminished as the proportion of dextrose was increased. The results of stage (b) prove that this was due to the relatively large proportion of nitrogen fixed as cyanate in accordance with equation (4). In the case of experiment 5, for example, 18.99 per cent. of the theoretical yield of cyanic acid was generated during the decomposition of the ammonium salt in the presence of the stated amount of dextrose. If the reaction under consideration is essentially an oxidation change, this result goes to show that a strong tendency must exist towards the realisation of equation (4). On the other hand, since alkaline hypobromite must act as a brominating agent as well, the formation of cyanic acid in the manner



must not be overlooked.

Any compound capable of yielding ammonia during its decomposition by 'alkaline hypobromite' would obviously tend to generate cyanic acid in the presence of dextrose. On comparing the values for stage (b) in experiments 1, 2, and 3 (Table I), with those in Table III, it will be seen that, all other conditions being equal, or nearly so, the proportion of nitrogen fixed as cyanate was distinctly higher when dextrose was present. Thus in this respect the sugar exerts a function the very opposite of that which it has been supposed to possess.

Considering that any easily oxidisable carbon compound is liable to give more or less carbon monoxide by the action of 'hypobromite,' the discordant results which have been obtained in the estimation of urea in urine by this method are not surprising.

An example of the results obtained with a sample of normal urine, when stage (b) was applied, is given below.

A. Urine (3 c.c.) added to excess of 'hypobromite.'

B. Hypobromite in excess added to urine.

Vol. of gas at N.T.P.

		Total.	Urea per cent.
A.	(a) = 21.90 c.c. (b) = 2.89 c.c.	24.79 c.c.	2.21
B.	(a) = 21.68 „ (b) = 2.82 „	24.50 „	2.18

Comparing the results with those for a 2 per cent. solution of urea (expt. 2, Table I), it is found that whilst with urine the ratio of nitrogen fixed as cyanate to nitrogen evolved in stage (a) is 1:7.57, it is 1:10.89 in the case of the plain urea solution. Whilst this difference has been confirmed by a number of experiments, the fact is merely recorded here. Its significance will be dealt with on another occasion.

#### *Urea and Neutral Hypobromite Solution.*

Sixteen grams of bromine were added to 50 c.c. of 4N-sodium hydroxide solution cooled to 0°; 15 c.c. of the solution were added to 0.06 gram of urea in 2 c.c. of water contained in the nitrometer. No gas was evolved after the mixture had remained for five minutes. On the addition of 2 c.c. of sodium hydroxide solution (20 per cent.), there was an immediate brisk evolution of gas equal to 12.1 c.c. at N.T.P. The yellow colour of the solution was destroyed and excess of urea remained. Had sodium hypobromite been formed in theoretical yield according to the equation  $2\text{NaOH} + \text{Br}_2 = \text{NaBrO} + \text{NaBr} + \text{H}_2\text{O}$ , 1.5 c.c. of the solution, after addition of alkali, would have sufficed to decompose the whole of the urea taken. The result shows that only slightly more than 5 per cent. of the theoretical amount of 'hypobromite' was formed. The estimation of the latter by the addition of an excess of urea is a more accurate process than the reverse operation, since the only source of error is due to the small amount of carbon-monoxide evolved.

Sixteen grams of bromine were added to 50 c.c. of 8N-sodium hydroxide solution, that is, to give  $\text{NaBrO}:2\text{NaOH}$ ; 2 c.c. of the solution were more than sufficient to decompose 0.06 gram of urea. The results obtained were: stage (a) = 19.9 c.c., stage (b) = 2.45 c.c., equal to 99.77 per cent. of the theoretical.

Thus whilst an excess of alkali is necessary to promote the form-

ation of the theoretical yield of sodium hypobromite as represented in the above equation, it is also essential to initiate the decomposition of urea. Neutral 'hypobromite' does not liberate nitrogen from urea in the cyclic form. A change to the configuration  $\text{HN:C(OH)NH}_2$  must precede the decomposition, which is no doubt the result of bromination, hydrolysis, and oxidation following each other with such great velocity as to be practically simultaneous.

When the reaction is slowed down, the proportion of cyanate formed is considerably increased, as shown by the following result. An excess of neutral 'hypobromite' was added to 0.06 gram of urea in 2 c.c. of water. No gas was evolved. Sodium hydroxide solution (20 per cent.) was gradually added until evolution of gas ceased.

Result: (a) = 15.74 c.c., (b) = 6.92 c.c. at *N.T.P.* Total = 22.66 c.c., or 101.1 per cent. of total nitrogen of urea. Approximately 30 per cent. of the nitrogen was fixed as cyanate during the decomposition of urea in stage (a) under the above conditions. The presence of carbon monoxide was responsible for the excess of gas over the theoretical.

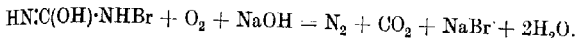
#### *The Mechanism of the Urea-Hypobromite Reaction.*

So far as the mechanism of this reaction is concerned, whilst rapid decomposition of an unstable bromourea formed in the first instance gives rise no doubt to the products of the main change, it is evident that the tendency of urea to decompose into ammonia and cyanic acid is a prominent feature of the reaction. The change in this direction is promoted by a low concentration of alkali, whereby the velocity of the reaction is reduced.

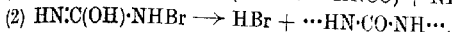
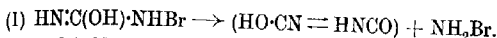
Schestakov's discovery (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 1) that hydrazine is formed when urea is attacked by alkaline sodium hypochlorite at about 5° has led to the suggestion that the oxidation of this substance represents the ultimate source of the nitrogen in the decomposition of urea by hypochlorites, or hypobromites in alkaline solution under the conditions usually employed. This view is not in agreement with the fact that the nitrogen fixed as cyanate is greatly increased when the velocity of the reaction is slowed down. As a matter of fact, sodium cyanate was formed in considerable amount in several repetitions of Schestakov's experiment.\* The evidence is in favour of the

\* With respect to the large yield of hydrazine claimed by Schestakov, this has never been confirmed. Experiments made in the author's laboratory gave a very much smaller quantity than that stated. This appears to have been the experience of others (compare Fenton, *Ann. Reports*, 1905, 2, 96).

view that hydrazine is the product, of a secondary reaction. For this reason the author is not inclined to give the attention which Hurtley (*loc. cit.*) has given to its formation in explaining the origin of carbon monoxide during the decomposition of urea by 'hypobromite.' A bromourea generated in the presence of alkali could have but an ephemeral existence. Simultaneous hydrolysis and oxidation would complete its decomposition, according to the equation



During the violent disruption of such a compound, it is conceivable that by-products may arise as a result of its direct decomposition in two different directions, thus :



Hydrolysis of  $\cdots\text{HN}\cdot\text{CO}\cdot\text{NH}\cdots$  at the moment of its generation would give rise to carbon dioxide and hydrazine, whilst incomplete oxidation would be represented by the change  $\cdots\text{HN}\cdot\text{CO}\cdot\text{NH}\cdots + \text{O} = \text{N}_2 + \text{CO} + \text{H}_2\text{O}$ . In the case of Schestakov's experiment, the formation of hydrazine from the interaction  $\text{NH}_3 + \text{NH}_2\text{Cl} = \text{N}_2\text{H}_4\cdot\text{HCl}$  must not be overlooked. It is during a violent reaction that one would expect carbon monoxide to escape oxidation. The facts support this conclusion. Krogh (*loc. cit.*) found a greater evolution of carbon monoxide when the 'hypobromite' was very rich in alkali, and Hurtley (*loc. cit.*) showed that much less of this gas was present with the nitrogen evolved from the decomposition of urea by a hypochlorite than by a hypobromite.

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## CCLXXXI.—*The Ultra-filtration of Soap Solutions: Sodium Oleate and Potassium Laurate.*

By JAMES WILLIAM MCBAIN and WILLIAM JOB JENKINS.

THE method of ultra-filtration as developed in the present paper not only supplies an independent check on data observed by other means, but also results in extensive additions to our knowledge of soap solutions. It will be shown that quantitative information with regard to the following may be obtained by the proper application of this method :

1. The relative amounts of crystalloid and colloid present.
2. The osmotic pressure of the solutions.



3. The hydrolysis of soap in solution.
4. A general method of determining the hydration of colloids in solution.
5. The theory of ultra-filtration.
6. The separation of ionic micelle from neutral colloid, and determination of the composition of the ionic micelle and the diameter of the various colloidal particles.

The subject-matter will be dealt with in the foregoing order, after description of the experimental method and a brief account of the theory involved. It will be seen that the results afford striking evidence in support of the theory of colloidal electrolytes. It is necessary very carefully to examine the experimental basis of all such work in view of the remarkably discordant conclusions of such investigators as Jacques Loeb, Pauli, Bancroft, Martin Fischer, Brailsford Robertson, and ourselves. Carefully established data should be of permanent significance.

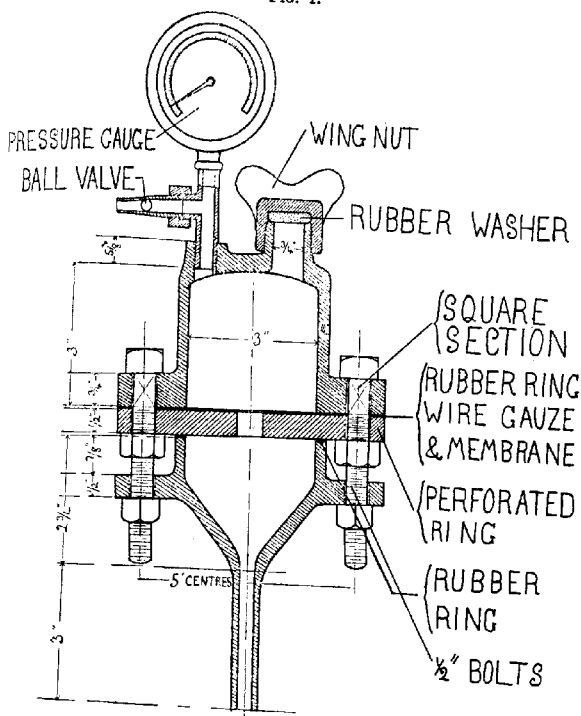
#### *The Ultra-filter.*

The design of the ultra-filter finally employed is shown in Fig. 1, which is a working drawing drawn to scale. It is a development of Hatschek's modification of that of Bechhold ("Laboratory Manual of Elementary Colloid Chemistry," Hatschek, 1920, p. 70). It was designed for use with much higher pressures than any hitherto employed; it may be surrounded by a thermostat, and the filtrate collected out of contact with the atmosphere or carbon dioxide. Finally, it lends itself to testing for absence of leakage and determination of the size of pores in the membrane without disturbing the latter, merely by removing the funnel underneath. The filter is  $6\frac{1}{2}$  inches in external diameter and is designed for pressures up to 900 lb. per square inch, but it was used up to pressures of only 500 lb. per square inch (thirty-three atmospheres); a higher pressure, such as 100 atmospheres, would be distinctly advantageous. It is made of heavily nickel-plated phosphor-bronze, and has a capacity of about 250 c.c., about 70 c.c. of soap solution being actually employed. The perforations in the filter plate consist of four holes, 1 inch in diameter (not shown in Fig. 1), around the centre hole, which is half an inch in diameter. The membrane was supported on nickel gauze, and  $\frac{1}{4}$ -inch rubber washers were used to render the joints air-tight. A cylinder of oxygen was used as the source of pressure. The membranes described in the present paper are useless for temperatures above 60°.

In the early part of the investigation, the analyses of the soap solutions were made by titration. In later work, a Zeiss dipping refractometer was invaluable, since only a few drops of soap

solution were required for an accurate determination of the concentration of the solution. All concentrations are expressed in terms of weight normality, referring to 1000 grams of solvent.

Fig. 1.



#### *Diameter of the Pores of the Ultra-filter.*

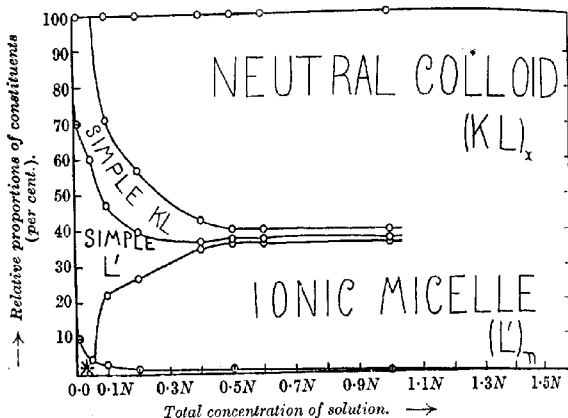
The methods used in preparing and testing the membranes are those of Bechhold (*Z. physikal. Chem.*, 1907, 60, 257; 1908, 64, 328); Schering's 10 per cent. glacial acetic acid collodion and a specially made 15 per cent. solution were employed, but it was found that a 15 per cent. solution prepared by ourselves made still denser membranes. Schleicher and Schüll filter-papers, No. 575, were used.

The most convenient method of estimating the size of pores is by determining the minimum pressure that will force air through

individual pores when the membrane is inverted under water. The diameter of the pore is inversely proportional to the minimum pressure required, being 300, 30, and 3  $\mu$  for 1, 10, and 100 atmospheres, respectively. The information generally obtained from this bubble-test is the diameter of the maximum pore and the diameter and number of pores of approximately the same magnitude as the maximum pore.

Contrary to impressions derived from the literature, it was found that the pores in any one membrane vary over a very wide range of diameter, and usually only the largest of these is accessible to measurement; for instance, in one membrane there was only

FIG. 2.



The relative proportions of the various constituents of solutions of pure potassium laurate at 18°. (The asterisk \* marks the field showing the proportions of acid soap, 2KL, HL, present.)

one pore as large as 300  $\mu$ , two being 150  $\mu$ , three 90  $\mu$ , six 75  $\mu$ , and eight 60  $\mu$ . It was more usual, however, to find about a dozen pores within 10 per cent. of the maximum pore. An indication of the diameter of the maximum pore in relation to the solution employed is given by the following data: our 15 per cent. 9  $\mu$ , Schering's 15 per cent. 18  $\mu$ , 10 per cent. 33  $\mu$ , 7.8 per cent. 90  $\mu$ , 5 per cent. 150  $\mu$ , and 3 per cent. 450  $\mu$ . (The value 9  $\mu$ , however, corresponds with the highest pressure available for testing, so that the pores must have been smaller, possibly much smaller.)

#### The Mobility of the Ionic Micelle.

In previous communications from this laboratory, the conductivity and osmotic activity of soap solutions have been studied

and a theory of colloidal electrolytes has been advanced. According to this, soap when in true solution behaves entirely as a crystalloid, but the undissociated soap may be aggregated to form particles of neutral colloid, whereas if the fatty ions are aggregated (without loss of electrical charge) they form colloidal particles known as the ionic micelle, which are supposed to contain some neutral colloid. On account of its well-known small molecular weight and the clear distinction between its behaviour in crystalloidal and colloidal form, soap is one of the best representatives for the study of the theory of this comprehensive group, lacking the ambiguity of the corresponding study of protein or of gelatin with their unknown molecular weight and basic and acidic functions (for reference see this vol., p. 621; also, "Third Colloid Report of the British Association for the Advancement of Science"; Salmon, this vol., p. 711). Figs. 2 and 3 embody the results which have been deduced by Miss M. H. Norris solely from conductivity and freezing-point data in the case of the two soaps studied in the present paper.\*

The concentrations ascribed to the ionic micelle depend directly on the mobility postulated for it. The total osmotic activity of a moderately concentrated solution of sodium oleate as measured by the freezing point is so small that even if the whole osmotic effect is ascribed to the sodium ion less than half the observed conductivity is accounted for, and it is necessary to postulate for the ionic micelle an equivalent conductivity at least equal to that of the potassium ion and therefore several-fold greater than that of the fatty ions from which it is derived.

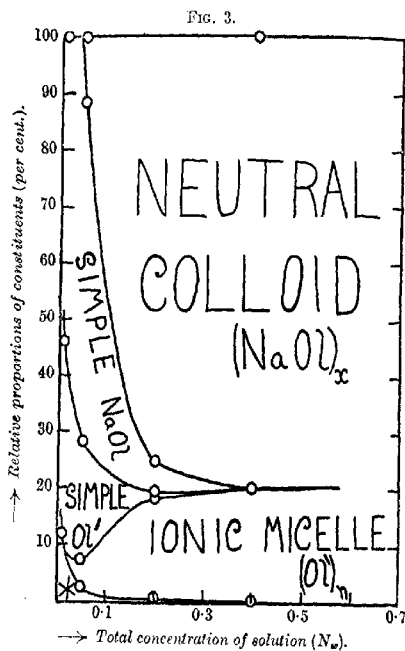
It is now seen from Fig. 3 that the concentrations deduced from this assumption leave, as the only constituents present in appreciable amount, neutral colloid, ionic micelle, and the equivalent amount of the sodium ion. This equilibrium is almost fully established in  $0.2N_w$ -oleate and it is almost unchanged on proceeding to  $1.4N_w$  and beyond. Potassium oleate, for which the data are fuller, presents very similar results. A method immediately arises for calculating the hydration of the total soap and checking the assumed value for the mobility of the ionic micelle. Accepting the type of equilibrium shown and assuming that the mobility of the ionic micelle and the number of molecules of hydrate water combined with or sorbed by one molecule of total soap is the same in  $0.4N_w$  and  $1.6N_w$  solutions, the following equations may be set up

\* The following values were involved in Miss Norris's calculations:—mobilities of the simple fatty ions = 20.7; ionic micelle =  $K' = 64.7$ ;  $Na' = 13.6$ ;  $OH' = 174$ ;  $k_{KL} = 0.22$ ;  $k_{NaOl} = 0.04$ . Five per cent. of the total oleate in the  $0.05 N_w$  solution was assumed to be present as ionic micelle.

to represent the conductivity and the lowering of freezing point, respectively. From the freezing point, the weight normality of the potassium ion referred to the true solvent water only is equal to  $t^\circ/1.858$ .

From the conductivity this true weight normality of the potassium ion is equal to

$$\frac{\mu_v}{u+v} \times \text{apparent } N_w \times \frac{h+s}{s},$$



The relative proportions of the various constituents of aqueous solutions of pure sodium oleate at  $18^\circ$ . (The asterisk \* marks the field showing the proportion of acid soap,  $2\text{NaOl}, \text{HOl}$ , present.)

where  $h$  is the hydrate water and  $h + s$  is the total water associated with one gram-atom of potassium and  $u$  is the mobility of the potassium ion, equal to 64.7. It is evident, by combining these two equations, that  $h$  and  $v$  are determined, since for  $0.4N_w$  and  $0.6N_w$ ,  $h + s_1 = 1667$  and  $h + s_2 = 2500$  grams of water.

Inserting numerical data, the mobility deduced for the oleate micelle is 77.9 mhos, and the hydration, 289 grams, equals 16 mols.

of water. The mobility thus appears to be even higher than that of the potassium ion, and the hydration is of the magnitude expected from the new data in the present paper (p. 2336) and from previous studies.

It is interesting to notice that we have now two lines of evidence which would indicate that at least eight or ten ions must be contained in one ionic micelle, since otherwise the osmotic pressure of the ionic micelle would be so appreciable as to affect the calculation in the direction of requiring a still higher mobility. Again, if the ionic micelle has a mobility only four times that of the laurate or oleate ion, the principle of Stokes's law would require an agglomeration of at least eight ions to account for this, even neglecting hydration; further, this becomes a minimum of ten ions if it is assumed that the osmotic pressure of one colloidal particle is the same as that of one ion or molecule. On the other hand, the general conclusion to be drawn from the present work on ultrafiltration is that ten is about the maximum number of ions contained in any one particle of ionic micelle.

#### *The Equilibrium Crystalloid $\rightleftharpoons$ Colloid.*

The crystalloidal constituents of a soap solution are simple undissociated soap such as potassium laurate, simple fatty ion ( $L'$ ), hydroxyl ion, and sodium ion. It will be shown that for our present purpose the hydroxyl ion is negligible, and only that portion of the sodium ion which corresponds to the simple laurate ion can be mechanically separated from colloidal ionic micelle. Hence, on filtration through a very dense membrane, only crystalloidal soap and its simple ions will pass into the filtrate, whilst both forms of colloids, namely, ionic micelle ( $L'$ ), and neutral colloid ( $KL$ ), will be held back. It is thus possible to obtain a direct experimental check on the conclusions arrived at in previous papers that there is a true, reversible equilibrium between all these constituents, and also to prove the numerical values thus assigned in Figs. 2 and 3.

According to Salmon (*loc. cit.*), a solution which is normal with regard to both potassium chloride and potassium laurate contains practically the whole of the soap in colloidal solution, chiefly as neutral colloid, although partly as ionic micelle. Using the densest membrane, it was found that no potassium laurate passed through. This result was supported by other experiments on  $0.6N_{\bullet}$  and  $0.5N_{\bullet}$  potassium chloride with  $1.1N_{\bullet}$  and  $1.5N_{\bullet}$  potassium laurate, respectively, where likewise the soap was all in colloidal form.

The filtrate from a solution which was  $0.233N_{\bullet}$  and  $0.103N_{\bullet}$  with respect to sodium oleate and chloride, respectively, contained

soap corresponding to not more than  $0.001N_w$ -crystalloidal sodium oleate.

When filtering  $0.493N_w$ -solutions of pure potassium laurate, it was found that the concentration of the filtrate was  $0.046N_w$ -potassium laurate, independent of the pressure (between six and twelve atmospheres). The fact that the concentration of the filtrate is independent of the pressure, even although there is a large range in the size of pores in the membrane, shows that the particles of ionic micelle and neutral colloid were distinctly larger than the largest pore in the membrane, demonstrating the sharp break in dimensions between colloid and crystalloid. Similarly, the concentration of the filtrate from sodium oleate was independent of the pressure.

Tables I and II present the results of filtration of the laurate and oleate through this dense membrane, which thus measures the total amount of soap present in crystalloidal form. In each case, the solution was first concentrated by filtration to the desired extent, thereupon the filtration was continued for many hours, returning to the solution from time to time the whole of the filtrate coming through in the hope that the final sample taken should nearly correspond with the equilibrium. The filtrate was analysed by the usual titration methods for laurate and potassium. Repetition of these experiments should give more accurate results, particularly if the refractometric method of analysis is employed. A careful study of the pressures should also be made so as to ensure that no crystalloidal soap is being held back, in accordance with the theory of ultra-filtration developed in a later section. The results deduced by other methods, described in previous communications, which are known to be inaccurate in the second decimal place, are given for comparison. It will be seen that the nature of the equilibrium is undoubtedly confirmed, and it becomes extremely difficult to question the main hypothesis of our theory of colloidal electrolytes. In both cases, all the soap is present in crystalloidal form in  $0.01N_w$ -soap solutions. With increasing concentration, the proportion of soap in crystalloidal form diminishes very rapidly. The  $0.01N_w$ -sodium oleate and potassium laurate were filtered immediately after being prepared. It is possible that the colloidal acid soap formed by hydrolysis had not agglomerated sufficiently to be held back.

#### *The Osmotic Pressure of Soap Solutions.*

Ultra-filtration permits of a determination of osmotic pressure, since, for any membrane that holds back any definite set of constituents, the osmotic pressure is the minimum pressure under

which filtration can occur. A strictly semi-permeable membrane is one which separates water from all the other constituents of the solution, and the minimum pressure required corresponds with results obtained by such methods as lowering of freezing point.

TABLE I.

Filtration of potassium laurate at 12–18° through a membrane with pores certainly less than  $9\ \mu$  in diameter, giving the concentration of total crystalloidal laurate soap.

Solution filtered.	Crystalloid.			Colloid.		
	A.	B.	C.	A.	B.	C.
0.01N <sub>w</sub>	0.01N <sub>w</sub>	—	—	0.00N <sub>w</sub>	—	—
0.174	0.028	0.06N <sub>w</sub>	—	0.146	0.11N <sub>w</sub>	—
0.210	0.042	0.06	—	0.15	0.15	—
0.277	0.043	0.05	—	0.234	0.23	—
0.313	0.044	0.05	—	0.269	0.26	—
0.370	0.045	0.04	—	0.335	0.33	—
0.493	0.046	0.02	0.04	0.447	0.47	0.46
0.547	0.048	0.02	—	0.499	0.53	—
0.679	0.052	0.04	—	0.627	0.64	—
0.750	0.052	0.06	—	0.698	0.69	—
0.808	0.052	0.07	—	0.756	0.74	—
0.998	0.054	0.12	—	0.944	0.87	—
1.000	0.054	0.12	0.07	0.946	0.88	0.93

A = by filtration; B = from conductivity and freezing-point data; C = from E.M.F. and freezing-point data.

TABLE II.

Filtration of sodium oleate at 12–18° through a membrane with pores certainly less than  $9\ \mu$  in diameter, separating colloid from crystalloid.\*

Solution filtered.	Concentration of filtrate.	Colloid retained.	Conductivity and freezing point.	
			Crystalloid.	Colloid.
0.01N <sub>w</sub>	0.01N <sub>w</sub>	0.00N <sub>w</sub>	—	—
0.144	0.001	0.143	0.02N <sub>w</sub>	0.12N <sub>w</sub>
0.188	0.001	0.187	0.01	0.18
0.227	0.001	0.226	0.01	0.21
0.349	0.0015	0.347	0.00	0.35
0.450	0.002	0.448	0.00	0.45
0.558	0.002	0.556	—	—

\* Although freezing-point data are lacking, E.M.F. measurements have given a value for the sodium ion in 0.06N<sub>w</sub> solution equal to 0.11N<sub>w</sub>, in agreement with the 0.12N<sub>w</sub> indicated in Fig. 3.

The most interesting case is obtained with the membranes described in the previous section, where all the crystalloidal constituents pass through while all the colloidal constituents together with the sodium ions equivalent to the ionic micelle, are retained. Here, the minimum pressure for ultra-filtration will be almost entirely due to the sodium ions and will afford a measure of the



ionic micelle as distinct from simple laurate or oleate ions. Finally, it is seen that with a coarse membrane which retains only neutral colloid, a few cm. pressure suffice to effect ultra-filtration. There are thus as many kinds and values of osmotic pressure as there are constituents in a solution, provided that the separation takes place at consecutive stages.

In practice there are two difficulties, one being the excessive slowness of ultra-filtration in the neighbourhood of the corresponding osmotic pressure, so that with the present apparatus the observed values would tend to be too great, even when the membrane is carefully watched for the first drops of filtrate. The other complication arises from the alterations and readjustments of equilibrium that take place in the filtrate, which of course directly affect the osmotic pressure. Hence, the only measurements added here are those referring to soap solutions in which the soap is entirely in the form of colloidal electrolyte.

In an experiment with 1.0*N*<sub>w</sub>-potassium laurate at 12–18°, no filtrate appeared in eleven hours with a pressure of 6.0 atmospheres, whereas two and a half hours later, with a pressure of 7.1 atmospheres, drops were collecting.

Table III gives the values thus obtained together with the concentration of sodium ions (equivalent to the ionic micelle) deduced therefrom, and for comparison, the concentration of ionic micelle deduced from conductivity and freezing point, and from *E.M.F.*, respectively. The agreement between the three methods is within the experimental error.

TABLE III.

Comparison of concentration of ionic micelle corresponding to minimum pressures required for ultra-filtration with values deduced by previous methods.

Solution filtered ( <i>N</i> <sub>w</sub> ).	Atmospheres required.	Ionic micelle.	From conductivity and freezing point.	From <i>E.M.F.</i>
0.4-K Laurate.	2.9	0.13	0.13	0.14
0.6-K Laurate.	4.7	0.21	0.21	0.20
1.0-K Laurate.	7.1	0.32	0.36	0.33
0.2-Na Oleate.	1.0	0.045	0.036	—
0.4-Na Oleate.	2.7	0.12	0.08	(0.07)

Bancroft, in propounding research problems in colloid chemistry (*J. Ind. Eng. Chem.*, 1921, **13**, 261), states that concentrated soap solutions show practically no rise in boiling point, and that this must be due to adsorption. His statement requires substantiation, since it directly calls in question all the data published from this laboratory on the osmotic activity of soap solutions by the four methods of vapour pressure, dew point, freezing point, and now

ultra-filtration, all of which show that soap solutions exhibit an osmotic activity about half that of sucrose or carbamide.

### *The Hydrolysis of Soap in Solution.*

The only previous determinations are those from this laboratory by *E.M.F.* and catalysis and conductivity measurements, all of which show that the concentration of hydroxyl ion is about 0.001*N* and that the other product of hydrolysis, in the case of sodium palmitate at 90°, is 2NaP,HP; further, investigations of a free acid incapable of hydrolysis, namely, hexadecanesulphonic acid, show that its behaviour in other respects is closely similar to that of the higher soaps (Norris, this vol., p. 2161). Bancroft, however (*loc. cit.*; also "Applied Colloid Chemistry," 1921, p. 225), considers that it should be possible, by analysing the filtrate in ultra-filtration, to prove a high degree of hydrolysis combined with adsorption of the sodium hydroxide in concentrated solutions. We confess inability to interpret the experimental data for soap solutions according to such an idea.

The hydrolysis-alkalinity as measured by ultra-filtration through the densest membranes, holding back all colloidal constituents, is shown in Tables IV and V. The alkalinity of the filtrate is determined by titration after adding four volumes of boiled-out alcohol.

TABLE IV.

Hydrolysis-alkalinity of potassium laurate solutions at 12–18° as measured by ultra-filtration.

Conc. of solution ( $N_w$ ).	Conc. of $OH'$ ( $N_p$ ).	Per cent. hydrolysis.	Conc. of solution ( $N_w$ ).	Conc. of $OH'$ ( $N_p$ ).	Per cent. hydrolysis.
0.277-K Laurate	0.0016	0.58	0.679-K Laurate	0.0012	0.18
0.370-K Laurate	0.0020	0.54	0.808-K Laurate	0.0010	0.12
0.493-K Laurate	0.0013	0.26	1.000-K Laurate	0.0009	0.09

TABLE V.

Hydrolysis-alkalinity of sodium oleate solutions at 12–18° as measured by ultra-filtration.

Conc. of solution ( $N_w$ ).	Conc. of $OH'$ ( $N_p$ ).	Per cent. hydrolysis.	Conc. of solution ( $N_w$ ).	Conc. of $OH'$ ( $N_p$ ).	Per cent. hydrolysis.
0.144-Na Oleate	0.0012	0.80	0.558-Na Oleate	0.0019	0.34
0.188-Na Oleate	0.0012	0.64	0.252-Na Oleate	0.0008	0.32
0.32-Na Oleate	0.0018	0.57	0.106-NaCl		
0.450-Na Oleate	0.0024	0.53			

The hydrolysis-alkalinity as determined by ultra-filtration is nearly the same as given by previous measurements at 90°. It was expected to be somewhat less, but the discrepancy, if real, is readily accounted for as the result of membrane hydrolysis (Donnan, *Z. Elektrochem.*, 1911, 17, 578), which would tend to exaggerate

the alkalinity found. The quantitative evaluation of the effective membrane hydrolysis is impossible without definite knowledge of the degree of solubility of the acid soap formed. Another circumstance which diminishes the accuracy of the results is that the laurate solutions were made by taking theoretical amounts of lauric acid. For this reason no stress can be laid on the results obtained and on the very similar results obtained with  $N_{\infty}$ -potassium laurate containing  $N$ -potassium chloride. Addition of 0.1N-sodium chloride to 0.25 $N_{\infty}$ -sodium oleate diminished the hydrolysis-alkalinity to 0.0008 $N_{\infty}$ -hydroxyl ions.

*The Hydration of Soap in Solution; a General Method.*

The hydration of soap may be defined as the total number of gram-molecules of water chemically combined with or sorbed by one gram-equivalent of the soap. This can readily be measured by ultra-filtration (McBain, "Third Colloid Report of the British Association for the Advancement of Science," 1920, p. 19) provided that a suitable indifferent reference substance is available. The extent of the increase of concentration of the reference substance found in the filtrate above that in the original solution is a measure of the water abstracted by the colloid from the solution. If membranes are used which allow one colloidal constituent to pass through whilst another is retained (see a later section), it should be possible to measure the hydration of each. In experiments cited in Tables VI and VII, in which the corresponding chlorides were used as reference substances, it is highly probable that these are slightly sorbed by the soap; if so, the true values for the hydration are correspondingly greater (compare T., 1921, 119, 1372, 1380, 1381, 1674). Further, the hydration in the absence of these salts should be distinctly greater.

These experiments constitute very direct proof that the soap in these solutions is colloidal and that it has the high degree of hydration predicted from earlier work.

TABLE VI.

Minimum values for the hydration per equivalent of potassium laurate in solutions at 12–18° in the presence of potassium chloride.

	$N_{\infty}$ of K Laurate.	$N_{\infty}$ of KCl.	Hydration found.
Earlier filtrate .....	0.000	0.762	11.8 H <sub>2</sub> O
Solution above .....	1.129	0.581	
Later filtrate .....	0.000	0.768	
First solution above .....	1.000	1.000	11.6 H <sub>2</sub> O
Filtrate .....	0.000	1.276	
Final solution above .....	1.056	0.991	

TABLE VII.

Minimum values for the hydration per equivalent of sodium oleate in solutions at 12—18°.

	$N_w$ of Na Oleate	$N_w$ of NaCl.	Hydration found.
First solution above .....	0.2517	0.1029	
Filtrate .....	0.0013	0.1077	9.2 H <sub>2</sub> O
Final solution above .....	0.2770	0.1028	

*Theory of the Ultra-filter.*

Excess of pressure inhibits ultra-filtration by stopping up the pores; with insufficient pressure, ultra-filtration becomes extremely slow or ceases altogether. It is only with suitably chosen intermediate pressures that deliberately planned ultra-filtration can be carried out and trustworthy information obtained regarding the diameters of the pores or filtered particles. Both the pressure used in the ultra-filtration and the osmotic pressure of the solution are decisive factors.

According to Bechhold (*Z. physikal. Chem.*, 1908, 60, 328), colloidion membranes only allow the passage of particles with diameters of not more than one-tenth that of the pores, but the evidence for his conclusion is speculative. It is difficult to ascertain the maximum ratio between diameter of particles passing through an ultra-filter and the diameters of pores as determined by the bubble-test. Bechhold's factor, one-tenth, is obviously a rough empirical correction for a number of factors operating under his experimental conditions.

Hatschek in collaboration with Bechhold has studied the effect of pressure on the diameter of deformable oil globules, which could be forced through pores measured by the air-bubble method (*Kolloid Z.*, 1910, 7, 86). He found that with high pressures oil drops could be forced through pores of diameter many times smaller than that of the drops themselves; he also concluded that the pores were not more than half the size indicated by the air-bubble test, but the precaution does not seem to have been taken of applying the air-bubble test after the ultra-filtration. Bechhold (*Kolloid Z.*, 1921, 29, 81), in filtering lecithin sols, obtained a similar increase in the amount of substance in the filtrate with increasing pressure.

The evidence goes to show that under suitably chosen conditions the diameter of the particles approximately corresponds with the diameter of the pores which just let them pass through. There is no indication in any of our observations that soap particles are deformable; indeed, we know of no reason for supposing that the

colloidal particles in soap solutions are of a liquid or emulsoid nature. Instead of more and more soap being forced through under high pressures, the filter becomes clogged to almost any desired extent. Bechhold mentions that Burian (*Arch. Fisiol.*, 7) has obtained a similar result with egg-albumin containing salt.

Of course, the relation between diameter of particles and of pores is much more complicated if the particles are not spherical. The length of a molecule of soap must be about 2 or 3  $\mu\mu$ , and this must be many times its breadth, and we have no information as to the form of either the ionic micelle or the neutral colloid. It will be shown that for practical purposes it is possible to express the size of each kind of colloid in terms of diameter of pores, and that the neutral colloid in the oleate is very many times coarser than the ionic micelle.

It is necessary to develop a theory of ultra-filtration, for non-deformable particles, as follows. Suppose we have a membrane with constant pores of every conceivable diameter up to and including a value  $a$  and, further, that there is in the solution a series of crystalloidal and colloidal constituents the diameters of which, from the coarsest to the finest, are equal to  $a, b, c, d$ , and  $e$ ,  $e$  being the water molecule itself, and that the partial osmotic pressures of the first four constituents are  $P_a, P_b, P_c$ , and  $P_d$ . It is obvious that only an infinitesimal pressure will be necessary to cause solution to flow through any pore the diameter of which is at least equal to  $a$ , so that a pore in diameter from  $a$  upwards would merely act as a leak. There are two principles involved in the action of all the other pores:

1. Only those constituents may pass through any given pore the diameter of which is less than the pore.
2. Nothing will pass through any given pore unless the pressure in use exceeds the osmotic pressure of every other constituent that is coarse enough to be held back.

There are thus two ways in which a given constituent may be prevented from passing through a given pore; namely, through the pore being smaller than the particle in question, or through the pressure in use not exceeding the osmotic pressure of some constituent of greater diameter than the pore in question.

The interplay of these two principles produces an unexpectedly complicated picture, but it will become apparent that there is a series of definite filtrates, each of approximately fixed concentration, obtainable with any given membrane, and each corresponding with a definite range of pressure. The whole range of conceivable pressures is therefore divided up by certain critical osmotic pressures, at which sharp breaks occur in the composition of the filtrate.

This definite composition follows, since, according to our hypothesis, only a definite set of pores will be functioning for all pressures lying between a pair of these critical osmotic values; for then, according to Poiseuille's law, the proportion of all the liquid flowing through, which is allotted to any one pore, remains independent of the total pressure. Between such a pair of pressures, altering the pressure merely alters the speed, so that the proportion passing through any one pore is only varied when, in consequence of a critical pressure being exceeded, additional pores are brought into play.

Turning now to the more detailed consideration of the membrane and the series of constituents postulated above, for all very low pressures filtrate I will be coming through pores of diameter  $a$  and will be merely unchanged solution; all pores of diameter less than  $a$  are out of action. As soon as the pressure exceeds the osmotic pressure  $P_a$ , pores lying between  $a$  and  $b$  will come into play; and the portion of the solution flowing through these pores will be deprived of constituent  $a$ , so that the gross composition of the filtrate can now be called filtrate II. The question as to whether pores lying between  $b$  and  $c$  are out of action or not depends entirely on whether  $P_a$  is greater than  $P_b$ ; if it is, then the pressure used has brought them also into action and they are contributing towards filtrate II, a solution deprived of both constituents A and B. Similarly, if  $P_c$  is greater than  $P_a$ , all pores smaller than  $c$  are out of action.

Filtrate III will then be reached when  $P_c$  is exceeded, and now we have pores of diameter  $a$  discharging unchanged solution, those between  $a$  and  $b$  holding back A only, those between  $b$  and  $c$  holding back both A and B, and those between  $c$  and  $d$  holding back A, B, and C, whilst if  $P_d$  is smaller than the critical value  $P_c$ , all pores, without exception, down to those of the diameter,  $e$ , of the water molecule itself, will be in action, those between  $d$  and  $e$  producing pure water. It does not matter even if  $P_d$  is the lowest osmotic pressure of all, pores smaller than  $d$  do not come into use until  $P_a$ ,  $P_b$ , and  $P_c$  are all exceeded.

For the membrane assumed, we have deduced three possible filtrates of fixed composition, I, II, and III. If none of the pores is quite as big as  $a$ , filtrate I is eliminated and no filtration will take place until the pressure in use exceed either  $P_a$  or  $P_b$ , whichever is the greater. Filtrates II and III are correspondingly altered in composition, since now they are not admixed with filtrate I. Similar reasoning applies if a denser membrane is used in which the diameter of the largest pores lies between  $b$  and  $c$ .

An illustration of these effects was given in a previous section,

where nothing passed through a dense membrane until the osmotic pressure of the ionic micelle and its accompanying sodium ions had been exceeded. Not even the crystalloidal soap or the simple laurate and potassium ions could come through, although their osmotic pressures were greatly exceeded; that is, until the osmotic pressure corresponding with the ionic micelle was reached. It is further evident that the filtrate must be at least slightly more dilute than corresponds to the crystalloidal matter in solution, since every pore, down to those of diameter  $e$ , must have come into action simultaneously, producing filtrate III.

In a soap solution, the coarsest constituent is the neutral colloid  $(\text{NaOl})_z$  or  $(\text{KL})_z$  with an osmotic pressure presumably equal to a few cm. only of water, so that filtrate II should be obtainable in any membrane the largest pores of which lie between neutral colloid and ionic micelle and only these pores can act. As a general rule, it should be stated that the only way to ensure that any constituent capable of passing through the filter is not separated from the corresponding solvent is to utilise pressures below the partial pressure of the constituent in question.

Theoretically, there should be a difference in composition between solution and filtrate when any solution whatsoever is being filtered under pressures which exceed the osmotic pressure of any constituent. Practically, the difference in the case of a crystalloidal solution would be slight unless the relative number of pores of diameter greater than  $d$  is severely limited.

Finally, apart from the possibility of deformable particles, there is one further complication which must be reckoned with in all work on ultra-filtration, and that is clogging of the pores, either mechanically or by adsorption. This, however, can be tested for by interrupting the experiment from time to time to carry out a bubble test. Tables VIII, IX, and X illustrate such clogging action, and the last also shows that high pressures may free the pores again temporarily. The data for filtrate III show the expected dependence of the composition on the individual membrane, but they also show a further deviation with pressure which indicates a real variation from Poiseuille's law.

#### *Separation of Ionic Micelle from Neutral Colloid.*

There are no colloidal particles of diameter larger than  $15 \mu$  in solutions of potassium laurate. In sodium oleate, on the other hand, the particles of neutral colloid all lie between  $75 \mu$  and  $450 \mu$ , whilst those of ionic micelle are definitely smaller than  $15 \mu$ . More accurate measurements in the separation of micelle from the neutral colloid in laurate solutions were not attained

owing to our not having foreseen the necessity of providing apparatus that would withstand the extreme pressures required for the bubble tests; and also because we had not developed in time the theory of the preceding section which is necessary to clear up the otherwise confusing data. All we can assert is that the ionic micelle both of laurate and of oleate is too large to pass through a membrane which showed no pores at all under a pressure of 33 atmospheres, which would have revealed any pores down to  $9\ \mu$ . The diameter of the ionic micelle is therefore not very many times the length of the laurate or oleate molecule.

The particles of neutral colloid correspond with diameter  $a$ , and those of ionic micelle with  $b$ . All pressures less than those found in the fifth section for the ionic micelle  $P_b$  should therefore yield filtrate II with membranes the largest pores of which measure between 15 and  $75\ \mu$ . It is proposed to show that this was the case with  $0.2N_{\omega}$ -sodium oleate, which consistently yielded a filtrate of  $0.04N_{\omega}$  with pressures less than  $P_b$ , and a more dilute filtrate when  $P_b$  was exceeded (filtrate III). For a given pressure, filtrate III is found to become more dilute as the pores get clogged. Since the osmotic pressure of the ionic micelle and its accompanying sodium ions so greatly exceeds that of the small amount of crystalloid present, filtrate III comes from three sets of pores producing pure water, solution of crystalloid, and solution of crystalloid plus ionic micelle, respectively. Typical data with membranes of different density are given in Tables VIII and IX. Of course, time is required to wash out the membrane and obtain a correct filtrate. The pore diameters given are those found by actual test during the course of the experiment. The diameters found with membranes that were contaminated with soap solution were calculated on the assumption that the surface tension was that of pure water. Such pores were therefore really smaller than here indicated.

TABLE VIII.

Filtration of  $0.2N_{\omega}$ -sodium oleate showing a constant filtrate of  $0.04N_{\omega}$  with pressures less than the osmotic pressure of the ionic micelle (one atmosphere), and a more dilute one when that is exceeded.

Series I.

Largest pore	$75\ \mu$							
Atmospheres	0.03	0.03	0.05	0.07	0.08	3	5	7
Filtrate $N_{\omega}$	0.040	0.040	0.040	0.040	0.040	0.035	0.027	0.020

Series II.

Largest pore	$75\ \mu$				$60\ \mu$		$45\ \mu$
Atmospheres	0.8	0.8	0.7		0.7	0.3	0.05
Filtrate $N_{\omega}$	0.015	0.040	0.040	0.040	0.040	0.040	0.040



## Series II (continued).

Largest pore	45 $\mu$							45 $\mu$
Atmospheres	3	3	3	5	5	0.7	0.7	0.7
Filtrate $N_w$	0.040	0.035	0.035	0.027	0.027	0.027	0.040	0.040

## Series III.

Largest pore	18 $\mu$							15 $\mu$
Atmospheres	5		0.8	0.7	0.5	0.3		0.05
Filtrate $N_w$	0.025		0.040	0.040	0.040	0.040		0.040

## Series IV.

Largest pore	75 $\mu$			60 $\mu$	45 $\mu$	18 $\mu$		15 $\mu$
Atmospheres	5	3	0.8	0.05	5	5	0.08	0.05
Filtrate $N_w$	0.027	0.035	0.040	0.040	0.025	0.023	0.040	0.040

TABLE IX.

Filtration of 0.296 $N_w$ - and 0.435 $N_w$ -sodium oleate showing a constant filtrate of 0.055 $N_w$  and 0.092 $N_w$ , respectively, with pressures less than the osmotic pressure of the ionic micelle (1.5 and 2 atmospheres).

Series I, with 0.296 $N_w$ -oleate.

Largest pore	75 $\mu$	75 $\mu$	75 $\mu$	60 $\mu$	45 $\mu$	45 $\mu$
Atmospheres	5	1.2	0.3	0.3	0.3	0.05
Filtrate $N_w$	0.033	0.055	0.055	0.055	0.055	0.055

Series II, with 0.296 $N_w$ -oleate.

Largest pore	300 $\mu$	75 $\mu$	75 $\mu$	75 $\mu$	75 $\mu$
Atmospheres		0.7	5	6.7	8.3
Filtrate $N_w$		0.055	0.033	0.029	0.020

Series III, with 0.296 $N_w$ -oleate.

Largest pore	300 $\mu$							
Atmospheres	6.7	6.7	6.7	5	5	0.7	0.7	0.3
Filtrate $N_w$	0.05	0.035	0.020	0.08	0.033	0.055	0.055	0.055

Series IV, with 0.296 $N_w$ -oleate.

Largest pore	300 $\mu$							
Atmospheres	5	5	5	6.7	6.7	6.7	1.2	0.3
Filtrate $N_w$	0.07	0.085	0.033	0.033	0.09	0.06	0.055	0.055

Series V, with 0.435 $N_w$ -oleate.

Largest pore	75 $\mu$	75 $\mu$	75 $\mu$	60 $\mu$	45 $\mu$	45 $\mu$	45 $\mu$
Atmospheres	2.7	1.8	0.3	1.3	5	1.3	0.3
Filtrate $N_w$	0.06	0.092	0.092	0.092	0.04	0.092	0.092

In Table X and XI are given data which throw light on the maximum diameter of the particles of neutral colloidal sodium oleate; these are certainly all smaller, and probably several times smaller, than 450  $\mu$ , and certainly all larger than 75  $\mu$ . Much lower pressures should have been employed. As in Table IX, Series III and IV, the filtrates increased in concentration to a maximum and then fell off as the pores were clogged.

TABLE X.

Maximum concentration of filtrates from 0.296 $N_w$ -sodium oleate, and ascertained diameter of largest pore at that time.

Pressure (atms.).	Largest pore.		Filtrate $N_w$ .	Pressure (atms.).	Largest pore.		Filtrate $N_w$ .
	Initial.	Final.			Initial.	Final.	
0.7	300 $\mu\mu$	75 $\mu\mu$	0.055	0.7	75 $\mu\mu$	70 $\mu\mu$	0.055
5	75 $\mu\mu$	150 $\mu\mu$	0.085	5	300 $\mu\mu$	150 $\mu\mu$	0.085
7	75 $\mu\mu$	150 $\mu\mu$	0.09	7	300 $\mu\mu$	150 $\mu\mu$	0.09
8	75 $\mu\mu$	300 $\mu\mu$	0.20	9	300 $\mu\mu$	300 $\mu\mu$	0.20

TABLE XI.

Filtrates from sodium oleate solutions through coarse membranes.

Solution. $N_w$ .	Filtrate. $N_w$ .	Largest initial pore.	Pressure (atms.).
0.21	0.21	450 $\mu\mu$	—
0.40	0.40	450 $\mu\mu$	—
0.30	0.20	300 $\mu\mu$	8
0.30	0.09	150 $\mu\mu$	7

#### *Concentration and Composition of the Ionic Micelle.*

In the preceding section there has been conclusively shown a definite separation of the colloidal constituents of sodium oleate solutions. At least 95—98 per cent. of the ionic micelle must have appeared in the filtrates, since they came through unaltered with pressures as low as 0.05 atmosphere. Again, the filtrate is the same when there are no pores larger than 15  $\mu\mu$  as when some equal 75  $\mu\mu$ , which shows that unless some of the particles of ionic micelle are very many times larger than all the others, they must all be of nearly equal dimensions. Similar reasoning shows that all the particles of neutral colloid existing independently of the particles of ionic micelle must be greater than 75  $\mu\mu$  in diameter.

We have, then, from 0.214, 0.296, and 0.435 $N_w$ -sodium oleate, constant filtrates of 0.040, 0.055, and 0.092 $N_w$ , respectively, which must contain ionic micelle and crystalloidal matter only. The crystalloidal matter is mostly sodium hydroxide and it is less than 0.001 $N_w$  (the corresponding particles of acid soap are probably coarse and cannot exceed a few thousandths normal).

Since the gross composition of the ionic micelle is given by these filtrates, and since we already know its concentration in electrochemical equivalents (see Table III), we can at once inquire as to how far the ionic micelle consists merely of aggregated oleate ions and in how far these are contaminated with neutral colloidal oleate. The data are given in Table XII, and it is at once seen that the ionic micelle is mainly composed of aggregated (and hydrated) oleate ions and that most of the neutral colloid exists in quite separate particles.

TABLE XII.

Concentration of ionic micelle and of neutral colloid, respectively, in sodium oleate solutions as found by ultra-filtration, compared with aggregated oleate ion and neutral colloid as deduced from conductivity and freezing-point methods; showing that they are present as two distinct sets of particles.

Solution. N <sub>m</sub> .	Ultra-filtrate.		Conductivity and freezing point.	
	Ionic micelle.	Neutral colloid.	(OI') <sub>n</sub> .	(NaOI) <sub>n</sub> .
0.214	0.040	0.174	0.038	0.176
0.296	0.055	0.241	0.055	0.241
0.435	0.092	0.343	0.087	0.348

A conclusion from much of our recent work is that perhaps the most important difference between the various soaps arises from the widely differing amounts and properties of neutral colloid, that is, un-ionised colloidal electrolyte, which we have now shown to be separate from the ionic micelle.

#### Summary.

1. A theory of ultra-filtration through permeable and semi-permeable membranes has been developed.
2. Ultra-filtration of potassium laurate and sodium oleate has confirmed the values, deduced by other methods described in previous communications, for hydrolysis, osmotic pressure, and amounts of crystalloidal and colloidal matter.
3. A general method for determining the solvation of the colloid by ultra-filtration has been described, and it has been shown that soap in solution contains at least 10 molecules of hydrate water per equivalent of soap.
4. The ionic micelle has been separated from neutral colloid by ultra-filtration; the diameter of the particles of ionic micelle is only a few times the length of the molecule, and its approximate formula is  $(OI')_{10}.mH_2O$ . Whereas the particles of neutral colloid of potassium laurate are less than  $15 \mu\mu$  in diameter, those of sodium oleate are about ten times larger.

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CCLXXXII.—On Dopplerite. *Studies in the Composition of Coal.*

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WE believe that considerable insight into the mode of formation and constitution of coal, and in particular of certain portions of bituminous coals, can be obtained from a study of that peculiar material to be found in peat-bogs, to which the name "dopplerite" has been given. Unfortunately, this material belongs to that class of compounds, the ulmin compounds, the colloidal nature of which is so discouraging to the chemist. For this reason, no doubt, information regarding the composition and properties of dopplerite is scanty and scattered, although descriptive accounts of it are numerous in the literature of coal. It will be necessary for us to review shortly the information that is available.

As early as 1839 reference was made to peculiar deposits in the peat-bogs of the Fichtelgebirge by Reinsch (*J. pr. Chem.*, 1839, 16, 489), who alluded to them as "Pechtorf" in contradistinction to "Rasentorf" (ordinary peat), but no detailed examination of them was made until 1849, when Doppler had his attention directed to one in a peat bed at Aussee, in Tyrol, and thought it of sufficient importance to warrant investigation. It was described as a black, gelatinous substance, occurring in layers about 10 feet in thickness 6 or 8 feet below the surface of the bog.

Doppler's examination of the black jelly (*Sitzungsber. Akad. Wiss. Wien*, 1849, 3, 239) showed it to contain a high proportion of water (it lost 80 per cent. of its weight on drying) and when anhydrous to be a brittle, shining, black substance with a conchoidal fracture. The fresh substance, on exposure to the air, lost its moisture rapidly and became elastic and of the consistency of indiarubber; it was insoluble in water, sparingly soluble in alcohol and ether, but readily soluble in a solution of potassium hydroxide.

A further examination of material from the same source was made by Schrötter (chemical) and Haidinger (microscopical), who confirmed and added to Doppler's observations (*ibid.*, p. 285). Haidinger observed that thin sections showed no trace of crystalline substances when viewed by polarised light, but that under high magnification traces of fibres of organic origin could be discerned. This latter statement, and the fact that the material in bulk was not uniformly glossy and of a dark-brown, almost black, colour, but contained dull streaks of a lighter brown, indicate that the

sample Haidinger examined was not as pure a specimen as that which has come to our notice. It was Haidinger who suggested the name of "Dopplerite," in honour of Doppler, for the material, and by this name similar jelly-like deposits in peat-beds have since been called.

Von Gümbel (*Neues Jahrbuch*, 1858, 278) laid stress on the character of the ash in dopplerite (which he regarded as a "homogeneous peat"). The ash in a specimen from Berchtesgaden, amounting to 1.67 per cent., consisted chiefly of lime, which von Gümbel believed to be in combination with the organic constituents.

A detailed study of the dopplerite from the original source at Aussee was made by Demel in 1883 (*Sitzungsber. Akad. Wiss. Wien*, 1883, 86, 872). Demel's analysis (C = 56.5; H = 5.75 per cent.) differs from most other records, both before and since, in showing no nitrogen. The ash, which amounted to 5.1 per cent., contained 73 per cent. of lime, which, as von Gümbel had suggested, seemed to be in combination with an organic constituent of the dopplerite.

In the same year, Fröh published a monograph entitled "Ueber Torf und Dopplerite" (Zürich, 1883), which reviewed the earlier work and described specimens of dopplerite from various sources. We reproduce a table of analyses given by Fröh, with additions (Table I).

TABLE I.

## Analyses of dopplerite.

Source.	Analysis. Percent. (ash-free and dried at 110°, unless otherwise stated).					Analyst.
	Ash.	C.	H.	O.	N.	
Aussee (dried at 100°)	5.86	51.11	5.30	42.40	1.09	Schrötter (1849).
Aussee	5.10	56.46	5.76	37.78	nil	Demel (1882).
Aussee	5.18	55.94	5.20	38.86		Kaufmann and Muhlberg (1865).
Obbergen	14.32	57.82	5.40	36.77		"
Obbergen	9.77	55.90	5.14	38.96		"
Obbergen	5.20	55.65	6.29	38.06		"
Dachmoos (dried at 130°)	5.39	57.47	5.32	36.35	0.86	Herz (1861).
Gonten	4.20	58.25	5.01	36.74	nil	Mayer (1861).
Gonten	4.42	55.55	5.64	38.28	0.57	Fleischer (1861).
Aurich	2.23	57.76	5.81	34.16	2.27	"
New Mexico	53.5	56.04	6.76	35.16	2.04	Foster (1913).
Sluggan Bog, Co. Antrim	5.12	58.49	5.38	34.72	1.41	Moss (1905).
Sluggan Bog, Co. Antrim.						
(a) Brilliant jelly	5.05	56.71	4.92	37.27	1.10	* Tideswell and Wheeler (1922).
(b) Dull jelly	5.2	57.91	5.31	34.68	2.10	* " "

\* The material also contained sulphur 0.70 per cent.

Moss (*Sci. Proc. Roy. Soc. Dublin*, 1903, **10**, 1, 93) has examined a dopplerite from the Sluggan Bog, Co. Antrim, Ireland, which resembled in all aspects those found on the Continent.

Dopplerite belongs to the group of substances, resulting from the natural decay of vegetable matter or prepared artificially from organic materials, to which the name "ulmins" or "ulmin substances" has been given. A discussion of the nature of these compounds, as disclosed by the researches that had been carried out up to the spring of 1917, appears on pages 32 to 36 of Stopes and Wheeler's "The Constitution of Coal" (H.M. Stationery Office, 1918), which should be consulted regarding the earlier work. A comprehensive review of the subject has also been given by Odén (*Koll. Chem. Beihefte*, 1921, **11**, 75). In contravention of the view that was at one time prevalent that the acidic reaction, and the power of combining with alkalis, that is possessed by ulmin substances, is a manifestation of their colloidal nature (see Baumann, *Mitt. bayr. Moorkulturanstalt*, 1909, **3**, 52; Baumann and Gully, *ibid.*, 1910, **4**, 31), Odén (*Proc. Faraday Soc.*, 1921), by applying physico-chemical methods of analysis, such as their potentiometric titration, was able to prove their true acidic character.

An interesting development of the subject is the preparation of furan- and phenol-ulmins. In a manner similar to their preparation from sugars, ulmins may be obtained from furan and its derivatives and from phenolic and similar organic compounds. Eller and Koch (*Ber.*, 1920, **53**, [B], 1469) and Eller (*Brennstoff Chem.*, 1921, **2**, 129), by oxidising phenols in alkaline solution, obtained ulmins which they regarded as closely resembling in chemical properties the natural ulmins; this led them to attribute the acidic character of the latter to the presence of phenolic hydroxyl groups. Marcusson (*Ber.*, 1921, **54**, [B], 542), starting with the assumption that the ulmins possess a nucleus with a furan structure (*Chem. Ztg.*, 1918, **31**, 237), succeeded in synthesising ulmins by the treatment of furan derivatives and furan itself. The synthesis, in Marcusson's opinion, involved the formation first of succindi-

aldehyde, then of a peridifuran,  $\begin{array}{c} \text{CH}_2\text{CH} \text{---} \text{CH} \cdot \text{CHO} \\ | \qquad \qquad | \\ \text{O} \qquad \qquad \text{O} \\ | \qquad \qquad | \\ \text{CH}_2\text{CH} \text{---} \text{CH} \cdot \text{CHO} \end{array}$ , and finally

of ulmin. The natural ulmins, according to this scheme, are formed by the conversion of cellulose, through levulose, into hydroxymethylfurfuraldehyde.

Our knowledge up to date of the constitution of the ulmins is limited to the recognition of the presence of certain reactive groupings in the molecules, which are undoubtedly large and complex.

Their acidic character can best be expressed by Berthelot and André's (*Ann. Chim. Phys.*, 1892, [vi], 25, 364) statement that ulmin is the anhydride of a polybasic acid and partakes of the nature both of an acid and an alcoholic anhydride. The ready esterification of the ulmins, and the evolution of carbon dioxide from them on moderate heating, are sufficient evidence of the presence of carboxyl groups.

All ulmins, from whatever source, yield protocatechuic acid on fusion with potassium hydroxide, thus indicating that they contain

the grouping  $\begin{array}{c} \text{O} \\ | \\ \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \text{O} \end{array}$ , which is present also in the lignone

portion of the lignocelluloses, and in tannins. From Roger and Vulquin's (*Compt. rend.*, 1908, 147, 1404) study of ulmin from peat, which they made with a view to discover some relationship with the pecto- and ligno-celluloses from which it is presumably derived, it is possible also to deduce the presence of (1) alcoholic hydroxyl groups (as in cellulose), (2) the acetyl grouping,  $\text{CH}_2\text{CO}$ , and (3) certain other characteristics of the lignone complex; and to affirm the absence of pentosans and hexosans. To this may be added the evidence of Robertson, Irvine, and Dobson (*Biochem. J.*, 1907, 2, 458) that, as in lignocelluloses, alkyloxy-groups (for example,  $\text{OCH}_3$ ) are present.

Fischer and Schröder (*Brennstoff Chem.*, 1921, 2, 37) believe the natural ulmins to be phenolic, and not carboxylic, in character, and to be derived entirely from the lignone portion of the lignocelluloses, which is of aromatic structure as distinct from the furan structure of cellulose. Artificial ulmins (such as sugar-ulmin), Fischer and Schröder consider to be different from natural ulmins and to contain a furan complex, since, like cellulose, they yield furancarboxylic acids on oxidation under pressure; lignone under this treatment yields aromatic carboxylic acids. Although Fischer and Schröder's opinions regarding the constitution of the ulmins apparently differ so markedly from those of Marcussen, the latter has shown that there is a connexion between the furan structure which he postulates (peridifuran ring) and the aromatic (phenolic) structure suggested by Eller and Koch (cyclohexane ring with an oxygen bridge).

The conditions of existence of the nitrogen that is present in all natural ulmins remain to be considered. The work of Maillard (*Ann. Chim. Phys.*, 1916, [ix], 5, 258; 1917, [ix], 7, 113) is most suggestive in this connexion. It seems clear that the nitrogen is derived from the degradation products of proteins, and exists in the condensed ulmin molecule essentially in closed  $\begin{array}{c} \text{---C---} \\ \text{---C---} \end{array} \text{N}$  rings,

although some may occur as imino ( $-\text{NH}$ ) groupings in the residual straight-chain structures of the reacting polypeptides.

*The Constitution of Dopplerite.*

Most of our information regarding the constitution of dopplerite is obtained from a study of the products of decomposition by heat of the dried material, as described in the experimental portion of this paper. The main products of decomposition, as with the ulmins in general, are carbon dioxide and water. The former undoubtedly arises, for the most part, from carboxylic acid (or anhydride), the latter from alcoholic hydroxyl groupings; both are eliminated at low temperatures, below  $300^\circ$ , leaving a residue containing little, if any, free carboxyl (anhydride) or hydroxyl groupings, although ethereal, ester, and lactone groupings remain.

The elimination of water between  $90^\circ$  and  $270^\circ$ , assuming that it all arises from hydroxyl groupings, accounts for 28 per cent. of the hydroxyl, and would leave behind 13 per cent. of ethereal oxygen ( $>O$ ), calculated on the original dried dopplerite. The carbon dioxide evolved over the same range of temperature is equivalent to about 8 per cent. of carboxyl; and above  $270^\circ$  carbon dioxide, equivalent to a further 4 per cent. of carboxyl, is evolved, although it probably arises from ester and lactone groupings, either present originally or formed during the earlier decompositions. Such groupings would also account for some of the water evolved at the higher temperatures, for the production of gaseous unsaturated hydrocarbons over the range  $250$ — $500^\circ$ , and possibly also for the liquid unsaturated hydrocarbons found in the distillates.

Acetic acid, which is evolved at low temperatures, gives evidence of the presence of an acetyl grouping; and methyl alcohol is derived from a methoxyl group, the methoxy-content of the dopplerite, as determined by Zeisel's method, being 0.75 per cent. (on the ash-free, dry substance). The nitrogen in dopplerite is firmly linked; easily decomposable imino-groups ( $>\text{NH}$ ) are not present in any quantity, whilst the pyridine groupings ( $\gg\text{N}$ ), which are probably present, must be firmly attached to large molecules.

In general, our examination of dopplerite shows its constitution to conform with that of the ulmins as disclosed by the work of Roger and Vulquin (*loc. cit.*). We see no reason to argue, with either Marcussen or Fischer and Schröder, the survival in the ulmins or, therefore, in dopplerite, of one type of molecular structure, originally present in the plants from which the ulmins are derived, or the exclusion of another type; to argue, for example, the survival of the lignone complex to the exclusion of the cellulose, or



*vice versa*; and we conclude that dopplerite is essentially a mixture of acid anhydrides of similar type.

The chief constituents, derived from the degraded celluloses, lignocelluloses, and proteins condensed together (as with the amino-ulmins) and dehydrated, still preserve the original lignone and cellulose groupings. There are also present in these chief constituents new ringed compounds, some of which contain the group-

ings  $\begin{array}{c} \text{—C—} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$  and  $\begin{array}{c} \text{—C—} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$ . Much of the original hydroxyl (alcoholic)

groupings remains unaltered, whilst a proportion has formed anhydrides (ethers) and some has condensed with the carboxylic groupings present to form esters and lactones. Incidentally, there are present constituents, extractable in small quantity by organic solvents, representative of the original oils and waxes of the plants, or their decomposition products.

#### *The Mode of Formation of Dopplerite.*

From their earliest recognition, the natural ulmins have been regarded as the products of decay of vegetable matter. The parts of plants that may undergo the processes of decay are varied in character: xylem, parenchyma, phloem, mesophyll, epidermis, cork, etc., can all, presumably, contribute to the formation of ulmic substances provided that decay, by whatsoever means induced, is carried far enough.

The mode of formation of modern peat-bogs, in which dopplerite is occasionally found, has received much study. Peats occur wherever vegetable debris is able to accumulate under suitably moist conditions. The deposition and accumulation of the debris is, in some instances, exceedingly slow; in others, it is more rapid. Some of the bogs are of considerable thickness, thirty feet or more, and it is known that some of the earliest formations date back to the Glacial epoch. When considering the reactions that may occur during the process of peatification, therefore, time must be recognised as an important factor.

The types of plants which may accumulate and decompose, forming peat, are many and diverse. In a single peat-bog each layer may be composed of a different type of plants, each of which may have grown and accumulated under different conditions. It is usual to divide peat-bogs into two main classes, the Upland and the Lowland. The former are chiefly composed of sphagnum moss and heather, so far as present-day additions to them are concerned; the latter are not now formed from mosses to an important extent, but are mainly from the *Cyperaceæ*, and from grasses of many varieties. During the formation of a peat-bog, each epoch had its

characteristic vegetation, of which, apparently, certain types predominated as peat-forming materials. Sometimes the growth of timber has alternated with that of mosses or bog-plants, and then well-preserved beds of timber are preserved in the bog, protected from extreme decay by the overlying peat.

Of the changes which occur in the decaying peat-forming material immediately after its deposition, decomposition by bacterial action is generally agreed to be of predominating importance. The extent of this action would appear to depend on local circumstances; in some instances the vegetable structures are left almost intact, in others decomposition and disorganisation of the plant morphology is complete.

It is generally assumed that the bacterial action causes its own defeat, the accumulation of products of the action antagonistic to bacterial life automatically ending the attack. It is, however, unlikely that the antiseptic property of the products of bacterial action on vegetable matter is the sole factor in determining the extent of that action. In many instances delicate and, presumably, most vulnerable tissues are found preserved intact in a matrix of disorganised material: in others, decomposition, to judge by the absence of morphological structures, is complete. Bacteria, then, if they were responsible for this complete decomposition, must have flourished in a high concentration of antiseptic material.

That bacteria have played an important part in the initial decomposition of plant deposits is certain. The portions first attacked are, usually, the soft-walled cells, consisting mainly of unchanged celluloses, and many of the more delicate tissues, together with the proteins and other cell-contents, which are, indeed, less resistant to attack than the cell-walls. The lignified, suberised, and cuticularised tissues, spore exines, resins, and waxes are more resistant to, some of them perhaps immune from, bacterial decay.

This view regarding the gradual decay, first of the less resistant plant structures and then, more slowly, of the more resistant, is borne out by all examinations of peat deposits; but the less resistant were not, apparently, always the celluloses and the proteins, for bacteria are known which attack the lignified tissues in preference to the unligified. When considering the probable action during the early stages of formation of the older peat deposits, therefore, the possibility of bacteria (not necessarily identical with present-day types) having shown variety in their choice of plant-structures to attack should be borne in mind.

The final products of bacterial action on plant debris are supposed to be the ulmins. Then, "regional metamorphism," in which

time, pressure, and temperature play their part, continues the peat-forming or coal-forming process.

Can it be assumed, however, without definite proof, that the ulmins are indeed the final result, or necessarily the result at all, of bacterial action? The unlikelihood, to say the least, of bacterial action persisting in a medium unfavourable to bacterial life would render any alternative explanation of the frequent complete ulmification of vegetable debris acceptable.

It is well known that ulmins can be formed under aseptic conditions; certain purely chemical and (superficially) simple reactions are known which yield ulmins differing, so far as has been ascertained, in no essential particular from naturally occurring ulmins. For example, Maillard's researches on the amino-ulmins have revealed a reaction, not dependent on bacteria, for the production of ulmins in nature of which it is difficult to believe Nature does not take advantage. This reaction, between carbohydrates and amino-acids, would occur as soon as the initial bacterial decomposition of celluloses, starches, etc., had produced materials of carbohydrate structure, and the decomposition of proteins had produced amino-acids. There the action of bacteria may be considered to end; thereafter, ulmification to be a chemical process.

Whatever be the agencies that produce the ulmins, the final result of the decay of vegetable matter, as exemplified by peat, is an accumulation of plant remains of great diversity of character, preserved more or less intact, surrounded by coatings, and separated by layers, of an amorphous material, the ulmins. The quantity of these compounds in a peat increases with its age, and sometimes accounts for the major portion of the mass.

Dopplerite, which is essentially an ulmin, is not a general, or even a frequent, constituent of peat-bogs. Observations regarding the occurrence of layers or accumulations of the brownish-black jelly, markedly different in appearance from the rest of the peat and therefore unlikely to be overlooked, have been few. The material must therefore be regarded as an abnormal result of peatification, and the conditions under which it occurs demand consideration.

Deposits of dopplerite are usually recorded as having been found in a peat-bog at some distance below the surface. Von Gümbel (*loc. cit.*) described the deposit at Berchtesgaden as lying chiefly between two layers of peat (Fasertorf and Specktorf) although veins of it ran upwards, suggesting that the material had at one time been fluid, or, being plastic, had been forced under pressure into crevices. Früh also considered that dopplerite had at one time been fluid, because he so frequently observed it in conjunction with twigs or roots, as though it had flowed along them, and in

crevices. From the description given by Lewis (*Proc. Amer. Phil. Soc.*, 1882, 20, 112) of a dopplerite deposit near Scranton in Pennsylvania, this also had been fluid.

The sample of dopplerite which we have examined, from Ireland, occurs about 10 feet below the surface of the bog in a layer about 3 inches in thickness, thinning off irregularly into the adjoining peat. Although physically it is so different from the peat with which it is associated, we consider that chemically the peat and the dopplerite are similar. Flecks of dopplerite, a centimetre or more in diameter, occur throughout the mass of some peats, and the older deposits consist largely of amorphous ulmins encrusting or lying between undecomposed plant tissues. Thus Kaufmann (*Jahrb. Geol. Reich.*, 1865, 15, 283) obtained from peat 9 feet below the surface of a bog 65 per cent. of material soluble in a solution of potassium hydroxide, and from an older peat 77 per cent.

Several hypotheses can be advanced to account for the distinctive form taken by the peat-ulmins when they appear as dopplerite. The view that the deposits are the result of complete bacterial decomposition and ulmification of vegetable matter, as distinct from the self-checked bacterial action which is supposed to have produced the main mass of peat, is unsatisfactory. Apart from our inability to conjecture what might be the factors that could encourage such localised bacterial activity, we question the possibility of any bacteria being able to remain active in a medium inimical to themselves during a length of time sufficient to transform the whole of the vegetable tissues into that inimical medium.

An alternative view is that dopplerite has arisen from peat ulmins that were deposited from solution. Fleissner (*Berg. Hüttenmannisches Jahr.*, 1919, Part I), in a discussion of the mode of formation of coal and of lignite, has suggested that the seeming absence of ulmins in coal may be accounted for by their having been leached out of the coal-forming materials by the action of alkaline solutions resulting from the disintegration of rocks. Whilst we do not uphold the suggestion that ulmins are absent from coal, we can imagine that some such action as Fleissner has postulated might have produced in peat local concentrations of ulmins in solution, later to be precipitated by chance acidification; for example, by a stream of water containing iron sulphate in solution. Such a sequence of events would account both for the form taken by dopplerite and for the high proportion of iron and of alkaline earths in its ash.

Another possibility lies in the formation of dopplerite masses *in situ* from solutions of amino-acids and carbohydrates produced from the accumulated vegetable matter by bacterial action. Such solutions would slowly interact, producing first water-soluble and

then insoluble ulmins. The presence of lime and alkalis in the ash of dopplerite would then be explained by the reactivity towards alkaline solutions evinced by the ulmins.

*Dopplerite in Relation to Coal.*

The general conclusion at which Stopes and Wheeler (*op. cit.*, p. 41) arrived regarding the constitution of coal, as a result of their examination of the evidence available, was that "coal is a conglomerate of morphologically organised plant-tissues, natural plant-substances devoid of morphological organisation (such, for instance, as 'resin'), together with the degradation products of a portion of the plant-tissues and cell contents comminuted, morphologically disorganised, or present in the form of varying members of the ulmin group."

With peat, ulmins extractable by a solution of potassium hydroxide may form 50 per cent. or more of the material; brown coals and lignites yield smaller quantities; whilst bituminous coals yield little or none.

Two views may be held to account for this gradually diminishing content of soluble ulmins. The one assumes that through polymerisation and dehydration (with the formation of anhydrides and lactones) the ulmins have been changed in character so as to lose their "characteristic" solubility in alkaline solutions; the other implies a difference in the mode of formation of the fuels. We incline to the former view, and consider that the amorphous cementing material for the numerous plant-structures in coal was originally a soluble ulmin, corresponding with the ulmins which surround and permeate the plant-structures in peat.

Is there, then, in coal any counterpart of the dopplerites—the localised accumulations of ulmins—in peat? There are several instances of the occurrence of masses of similar jelly-like materials in lignites; for example, John (*Verb. geol. Reichsanst.*, 1891, 64, 14) found in Bohemian lignite a black mass, resembling dopplerite in appearance and in its mode of occurrence, which he recognised as nearly pure ulmin, its analysis being: C, 55.00; H, 4.64; O and N, 40.40 per cent. No instances of the occurrence of dopplerite in bituminous and anthracitic coals are known; nor are they to be expected, for the solubility in alkaline solutions possessed by dopplerite is a transient property which time can destroy by such slight changes as result in the formation of anhydrides and in the loss of carbon dioxide from carboxyl groupings.

There is, however, in most bituminous coals a substance resembling dopplerite in many respects. This substance is "vitrain," the glistening black constituent of banded coals which has been

described by Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 470) and of which we have made a chemical examination (T., 1919, 115, 619). Vitrain has numerous points of physical resemblance to dopplerite: it has a brilliant surface lustre and a conchoidal fracture indicative of its existence at some time in a fluid state; and it is amorphous. Stopes (*loc. cit.*) refers to "its structureless nature, as of a hardened glue or jelly," and it is generally regarded as having been formed from a colloidal gel.\* Microscopic examination of thin sections fails to reveal a trace of organised structure.

A comparison between dopplerite and vitrain as regards their chemical compositions and their behaviour towards reagents shows the extent to which changes have been effected in the former during the process of coalification. The dopplerite we have examined, from an Irish peat-bog, and the vitrain, from Hamstead coal, can be compared as follows:

*Ultimate Analysis.*—

	Per cent. on ash-free, dry material.				
	C.	H.	O.	N.	S.
Irish dopplerite .....	57.9	5.31	34.6	2.10	0.70
Hamstead vitrain .....	78.5	5.15	13.9	1.36	1.12

\* The suggestion that bituminous coal, particularly the bright portions, is of a colloidal nature, and that certain bands in particular (which from the descriptions given of them seem to correspond with Stopes's vitrain) still possess the characteristics of a colloidal gel, is of some antiquity. The earliest reasoned exposition of this idea seems to have been that by Frémy (*Compt. rend.*, 1879, 88, 1048), although as early as 1807 Brongniart had conceived of coal as having been a homogeneous liquid, saying that it was "déposé ou formé étoit liquide homogène et dans un grand degré de finesse, ce que prouve sa texture souvent parallépipédique, et la manière dont il imbibé les couches qui l'enveloppent." (*Traité élémentaire de minéralogie avec des applications aux arts*, Vol. 2, Paris, 1807). One can believe, also, from his writings, that Hutton (*Theory of the Earth, with Proofs and Illustrations*, Vol. 1, Edinburgh, 1795) was imbued with the same idea.

Since these early times the notion of a "fundamental jelly" from which the mass of coal was formed has received the attention of a number of workers: for example, Bertrand (*Compt. rend.*, 1898, 127, 767); Grunmit and Hickling (*Proc. Manchester Phil. Soc.*, 1914); and Hickling (*Trans. Inst. Min. Eng.*, 1917, 53, 137); whilst the suggestion that particular portions of coal still retain some of the properties of a colloidal gel has been advanced by Potonié (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1908, 2, 48); Dowling (*Trans. Roy. Soc. Canada*, 1910, 4, 23); Porter and Ralston (*U.S. Bureau of Mines, Tech. Paper 65*, Washington, 1914); and Stopes and Wheeler (*The Constitution of Coal*, London, 1918), amongst others. From the general appearance and behaviour of vitrain, Stopes (*Proc. Roy. Soc.*, 1919, [B], 90, 470) regarded this particular portion of bituminous coal as essentially colloidal, as have all who have examined the substance since she described it; compare, for example, Tideswell and Wheeler (T., 1919, 115, 619); Lessing (T., 1920, 117, 256); Bone, Pearson, Sinkinson, and Stockings (*Proc. Roy. Soc.*, 1922, [A], 100, 582); and Stopes ("Fuel," 1922, 1, 22).

When the dopplerite was destructively distilled at low temperatures, large quantities of carbon dioxide and water were evolved; the composition of the residue then closely approximated to that of the vitrain, as follows: C, 78.35; H, 4.96; O + N + S, 16.75 per cent.

*The Action of Solvents.—*

Solvent.	Extractive matter, per cent.	
	Irish dopplerite.	Hamstead vitrain.
Chloroform .....	0.46	2.85
Alcohol .....	1.50	6.60
Pyridine .....	3.50	34.00
Aqueous potassium hydroxide...	93.00	6.10

With the gradual loss of carbon dioxide, acid compounds containing carboxyl groupings would tend to approximate more nearly in character to hydrocarbon structures, and an enhanced solubility in organic solvents would be expected. At the same time, loss of acidity would cause decreased solubility in alkaline solutions. Loss of hydroxyl groups would have similar effects.\* Already with dopplerite its solubility in alkaline solutions is less marked than that of the ulmin compounds in recent peat; solution is gradual, even on heating, and is not complete. This indicates that there has been some formation of anhydrides in dopplerite; although loss of carboxyl groups has only occurred to a small extent.

*Destructive Distillation.*—The presence of carboxyl groups in dopplerite causes carbon dioxide to be the principal gaseous product of distillation. Apart from this, the gaseous products from the dopplerite and the vitrain are similar and their composition varies with temperature in similar fashion (see Fig. 1, which should be compared with Figs. 1 and 2 in T., 1919, 115, 619).

The liquid products, although they differ in amounts, dopplerite yielding much water and but little tar and vitrain yielding much tar, have nearly the same character from both substances and are evolved at nearly the same temperatures. Both tars are essentially phenolic, that from the dopplerite being somewhat the less complex.

The similarity between the tars obtained from dopplerite and from vitrain is sufficient to show that both contain the same type of structure, a structure derived from the celluloses of the plants from which the ulmin compounds were formed. We consider that vitrain is similar to, but not identical with dopplerite, and that it

\* Professor Cobb has pointed out to us that if the gradual alteration in the constitution of any given ingredient of coal can be held to cause such a marked change in its behaviour towards solvents as is here suggested, any attempt to identify the original constituents of coal from a study of the action of solvents on coal is beset with difficulties; and that great caution is therefore necessary when drawing conclusions from such work regarding the nature of the coal conglomerate.

represents a more advanced stage in the process that has formed dopplerite from the decayed vegetation.

# EXPERIMENTAL.

The specimen of dopplerite which we have examined was obtained through the kindness of Professor Purcell. It occurs in the Sluggan Bog, County Antrim, Ireland. As received, the dopplerite was mixed with a considerable quantity of peat, from which, however, it could readily be separated. The jelly-like mass varied in texture; most of it had a dull appearance and freshly-broken pieces had a *matte* surface, but there was also a quantity of a brilliant black jelly the surface of which was uniformly glossy. The latter material was carefully separated from the dull jelly and used for the majority of our experiments; although the difference between the two varieties of dopplerite seems to be mainly one of texture, for on long keeping (in an air-tight receptacle) the dull material gradually altered in appearance, so that fractured surfaces of it were as brilliant as those of the original brilliant jelly. Analyses were as follows, calculated on an ash-free, dry basis, per cent.:

	Dull.	Brilliant.
Carbon .....	57.90	56.70
Hydrogen .....	5.31	4.92
Oxygen .....	34.00	36.60
Nitrogen .....	2.10	1.10
Sulphur .....	0.70	0.70

On drying artificially, the material shrank and hardened, and the brilliant jelly assumed the appearance of some naturally dried pieces which accompanied the sample embedded in fibrous peat. This naturally dried dopplerite was a hard, shining, black substance similar in appearance to polished jet, or to the vitrain of banded bituminous coals.

The undried dopplerite contained much moisture; the loss in weight on drying in a current of nitrogen at  $105^{\circ}$  was 74 per cent. The ash-content varied in different determinations between 3.5 and 5 per cent. The composition of the ash, obtained on incineration at  $700^{\circ}$ , is given in the table that follows, Demel's analysis of the ash from the dopplerite of Aussee being given for comparison:

Ash from Irish dopplerite.		Ash from Aussee dopplerite (Demel).	
SiO <sub>2</sub>	1.92 per cent.	}	12.02 per cent.
Fe <sub>2</sub> O <sub>3</sub>	17.32		
Al <sub>2</sub> O <sub>3</sub>	2.89		
MnO <sub>2</sub>	0.62		
CaO	56.96		72.67
MgO	4.27		2.03
Na <sub>2</sub> (K <sub>2</sub> )O	4.64		0.99
SO <sub>2</sub>	10.63		4.36
P <sub>2</sub> O <sub>5</sub>	traces		—
Cl	traces		1.09



One-third of the ash (of the Irish dopplerite) was soluble in water and the remainder was soluble in hydrochloric acid. The high content of lime, which was not in combination with an inorganic acid, agrees with the observations of others. The iron and the sulphur were partly in combination as sulphate; the main bulk of the ash was light grey in colour, but it contained flecks of red material in which the iron was concentrated.

*Acidity.*—The moist dopplerite was of distinctly acid reaction towards litmus paper. It was soluble for the most part in alkaline solutions, although with difficulty. A 15 per cent. potassium hydroxide solution was coloured dark brown when pieces of dopplerite were placed in it, but even after ten weeks much of the material remained undissolved. A quantitative determination of the solubility of the dopplerite in potassium hydroxide (5 per cent.) showed:

Soluble after ten days in the cold .....	37.5 per cent. (on dry material).
Soluble after further treatment during four hours at boiling-point .....	52.6   "   "   "
Insoluble residue .....	7.3   "   "   "

This slow rate of solubility points to the dopplerite being mainly a stable acid anhydride, and not an acid. The insoluble portion may be the result of change of the original dopplerite, due to loss of carboxyl, for example; or it may be an insoluble alkaline salt, or series of salts, such as have been observed with other ulmins (compare Berthelot and André, *loc. cit.*).

*Extraction with Organic Solvents.*—Five-gram samples of the dried material, pulverised and sieved through a 200 × 200 mesh sieve, were extracted in a Soxhlet apparatus (*a*) successively with different solvents, each extraction being continued during several days; and (*b*) with pyridine. The extract was separated by evaporation of the solvent in a vacuum; the quantities thus estimated were as follow:

(a) By chloroform .....	0.46 per cent.
By ethyl alcohol .....	0.96
By ethyl ether .....	0.12
By acetone .....	0.50
Total .....	2.04 per cent.
(b) By pyridine .....	3.50 per cent.

*Fractional Distillation. Gaseous Products.*—One gram of the dried material was heated in a vacuum, first at 150° and thereafter at intervals of 50° up to 600°, and the gases evolved at each stage of the heating were collected and analysed. Heating at each temperature was maintained during twenty-four hours, by the end of which time decomposition was complete. The results were as follow:

TABLE II.

Analyses of gases evolved at different temperatures.

Temperature ...	0—150°	200°	250°	300°	350°	400°	450°	500°	550°	600°
C.c. of gases at N.T.P. ....	—	5.0	12.4	23.0	21.0	16.8	16.1	21.9	31.9	40.0
Analysis, per cent. : Absorbed by conc. H <sub>2</sub> SO <sub>4</sub> .....	—	—	—	6.4	5.0	6.4	4.6	1.5	—	—
Carbon dioxide .....	92.3	83.7	72.7	67.0	47.6	25.2	13.0	9.0	3.5	0.7
Oxygen .....	0.4	—	0.2	0.2	0.1	0.3	—	—	—	—
Absorbed by bromine water .....	—	—	0.3	0.6	1.4	2.2	1.0	—	—	—
Carbon monoxide .....	5.7	15.4	19.8	23.7	30.9	34.7	29.1	21.4	21.2	23.7
Hydrogen .....	—	—	—	—	—	12.1	31.0	57.0	68.9	72.8
Paraffins .....	—	—	—	3.0	13.1	20.5	23.9	12.0	6.0	2.5
	98.4	99.1	99.4	99.5	99.5	99.6	99.5	99.4	99.6	99.7

The volumes of the principal gases evolved at each temperature, per gram of ash-free, dry material, were :

TABLE III.

Volumes of principal gaseous products. C.c. at N.T.P.

Temperature ...	0—150°	200°	250°	300°	350°	400°	450°	500°	550°	600°
Carbon dioxide	4.8	11.0	17.6	14.7	8.4	4.2	3.0	3.0	1.5	0.3
Carbon monoxide	0.3	1.9	4.8	5.3	5.6	5.9	6.7	7.2	8.8	10.0
Hydrogen	—	—	—	—	—	2.0	7.2	19.2	29.1	30.6
Paraffins	—	—	—	0.6	2.3	3.4	5.6	4.0	2.5	1.1

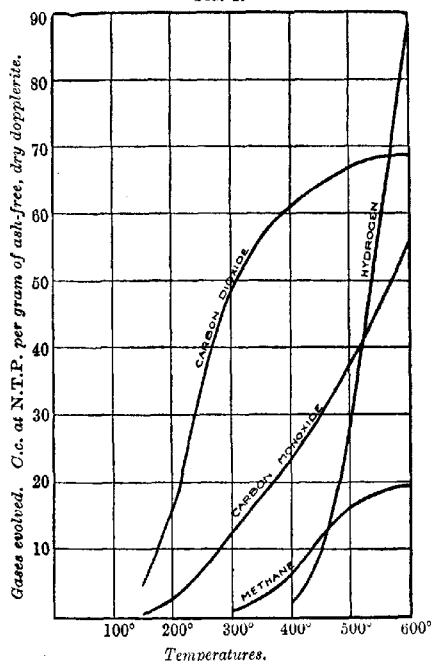
These results are recorded graphically in Fig. 1, from which the nature of the various thermal decompositions is apparent. The first gaseous products of decomposition are the oxides of carbon, carbon dioxide preponderating. The quantity evolved of the latter increases with increased temperature up to 250° and thereafter rapidly decreases, giving place to carbon monoxide, the evolution of which slowly increases up to 600°, the maximum temperature employed. Paraffins begin to make their appearance at 300° and are evolved in maximum quantity at 450°. Hydrogen, first observed over the range 350—400°, rapidly increases in quantity as the temperature is raised.

*Fractional Distillation. Liquid Products.*—The arrangement of the apparatus used was similar to that described by Jones and Wheeler for vacuum distillation (T., 1914, 105, 140), save that, instead of the spherical glass retort used by them, a cylindrical retort, 4 cm. in diameter and 20 cm. long, was employed. The material, which loosely filled the retort, was dried at 103° in an atmosphere of nitrogen and ground to pass a 10 × 10 and remain on a 30 × 30 mesh sieve; it weighed 120 grams.

The mode of procedure was to raise the temperature gradually, noting any evolution of gases or of liquids, and, whenever an obvious

decomposition point was reached, to maintain the temperature at that point until decomposition was complete. The distillation, throughout which a vacuum of about 10 mm. was maintained, lasted during three weeks. A number of fractions of liquid distillates were collected in an uncooled receiver and in receivers

FIG. 1.



cooled by a solution of solid carbon dioxide in ether, and were examined separately. The sequence of events was as follows:

Temperature.	Distillate.
90°	Copious evolution of water.
200°	Water, coloured light brown, but no oils. Gases, containing hydrogen sulphide in quantity.
250—270°	Water, coloured dark brown, with a little oil emulsion.
300°	Water and a light brown oil.
330—350°	A viscous, brown oil appeared at 330°. Much water still evolved.
360—400°	A viscous, red oil appeared at 360°.
400—450°	A little oil.
450—500°	A little oil.
500—550°	No further distillation of oils.

The residue remaining in the retort at the end of the distillation resembled closely the original dried dopplerite, although the pieces had shrunk slightly; it weighed about 55 grams, or 45 per cent. of the material taken for the distillation.

The distillates were separated for examination as follows (A), up to 90° (7 c.c.); (B), 90—270° (17 c.c.); (C), 270—410°; cooled receivers only (3 c.c.); (D), 410—550°, cooled receivers only (2.5 c.c.); (E), 270—550°, uncooled receiver (3 c.c.). Fractions D and E contained a small quantity of a crystalline substance, some of which also collected in the leading tube from the retort. This was chiefly ammonium carbonate, with some ammonium formate and ammonium chloride. Some viscous oils that had collected in the neck of the retort were extracted with ether and added to fraction E.

In each instance the aqueous portion of the distillate was examined for ammonia, acids, and furfural. The oils were separated by washing into basic, phenolic, and acidic fractions, which were examined separately. The results of the examination are shown in Table IV.

TABLE IV.

## Liquid distillation products.

Temperature.	Aqueous distillate.			Oils.			
	Percentages on original, ash-free, dry dopplerite.			Percentages on original ash-free, dry dopplerite.			
	Water.	Ammonia.	Acids.	Bases.	Phenols.	Acids.	Neutral Oils.
Up to 90° (Fraction A) .....	7.0	—	—	—	—	—	—
	(Some methyl alcohol, but no aldehydes, ketones, or organic acids.)						
Between 90° and 270° (Fraction B) .....	15.0	0.003	0.10	traces	nil	0.002	0.007
	(The acid had an equivalent 416; acetic acid was present, and furfural 0.036 per cent.)						
Between 270° and 410° (Fraction C) .....	2.5	0.002	—	traces	nil	0.002	0.015
	(Furfural was absent.)						
Between 410° and 550° (Fraction D) .....	2.0	0.004	—	Not examined.			
Between 270° and 550° (Fraction E) .....	1.7	0.040	0.01	0.02	0.65	0.023	0.30
	(Organic acids, equivalent 285, and a weak base present; no furfural.)						

Totals. Per cent. on original, ash-free, dry dopplerite: water, 28.0; ammonia, 0.05; bases, 0.02; phenols, 0.65; acids, 0.14; neutral oils, 0.32.

The outstanding feature of the distillation is the quantity of water evolved, amounting to 28 per cent. of the dry dopplerite. The production of water reached its maximum at about 270°, above which temperature it decreased rapidly. Between 90° and 270°, the aqueous distillate was acid owing to the presence of acetic acid and, in smaller quantity, of more complex organic acids; above 270°, the aqueous distillates became alkaline, and only traces of acids (including formic acid at the higher temperatures) were present. Ammonia was present in all the fractions, but chiefly in those obtained above 400°, as were the organic bases. Furfural was produced in small quantity (0.03 to 0.05 per cent.) below 270°, but was not observed in the distillates obtained at higher temperatures.

Cresols, distilling between 190–200°, were isolated from the phenolic portion of the oils, their quantity accounting for about 75 per cent. of the total phenols, which had the reactions of the simple phenols. No evidence was obtained of the presence of pyrocatechol or other of the polyhydroxyphenols.

A saturated hydrocarbon, m. p. 45°, was isolated from the neutral oils by fractional solution and crystallisation from pentane and alcohol. The neutral oils also contained a carbohydrate decomposition product; the remainder consisted of hydrocarbons, both saturated and unsaturated.

DEPARTMENT OF FUEL TECHNOLOGY,  
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### CCLXXXIII.—*Preparation of Sodium and Potassium Phthalimide.*

By DALZIEL LLEWELLYN HAMMICK and GEORGE HAZLEWOOD  
LOCKET.

THE preparation of the sodium and potassium derivatives of phthalimide by the original method of Landsberg (*Annalen*, 1882, 215, 181) is unsatisfactory in several respects. Thus the use of ethyl-alcoholic solutions of the metal hydroxides involves, in each case, large volumes of solvent and, in the case of sodium hydroxide, the presence of water as well. Good yields of sodium phthalimide cannot therefore be expected by the action of aqueous alcoholic sodium hydroxide on an alcoholic solution of phthalimide.

In order, therefore, to minimise the quantity of ethyl alcohol required, and, in the case of the sodium derivative, to avoid the

presence of water entirely, alcoholic solutions of phthalimide were treated with solutions of sodium or potassium ethoxide. The yields of sodium and potassium phthalimide thus obtained were by no means quantitative. On working, however, in amyl alcohol solution with sodium or potassium amyloxide, very nearly quantitative yields of the metallic derivatives were obtained.

*Sodium Phthalimide* (with ethyl alcohol as solvent).—Phthalimide (2.4 grams, previously dried in the steam-oven) was dissolved in 80 c.c. of ethyl alcohol (distilled from lime), the solution heated to its boiling point, and a hot solution of 0.6 gram ( $1\frac{1}{2}$  atoms) of sodium in 30 c.c. of ethyl alcohol added. When cold, the white precipitate was filtered off, washed with ether (dried over sodium), and dried in the oven. The alcoholic filtrate, treated with ether, deposited a further quantity of sodium phthalimide on standing over-night. The total weight of dry salt was 1.37 grams (50 per cent. of the theoretical yield) (Found: Na = 13.7. Calc., Na = 13.6 per cent.).

*Potassium Phthalimide* (with ethyl alcohol as solvent).—The procedure was the same as for the sodium derivative. The potassium ethoxide ( $1\frac{1}{2}$  times the theoretical quantity) was prepared by dissolving the potassium in alcohol diluted with dry ether, which was driven off when the solution was raised to boiling on the water-bath.

No further precipitate was obtained on treating the alcoholic filtrate with ether. The yield was 68 per cent. of the theoretical (Found: K = 21.3. Calc., K = 21.1 per cent.).

*Sodium Phthalimide* (with amyl alcohol as solvent).—The amyl alcohol used was distilled with benzene to remove water; the fraction used boiled at 129—129.5°.

Phthalimide (2.7 grams) was dissolved in 35 c.c. of amyl alcohol and treated hot with a hot solution of  $1\frac{1}{2}$  times the theoretical quantity of sodium in 30 c.c. of amyl alcohol. The precipitate was cooled, filtered, and washed with ether. No further precipitate was obtained from the filtrate with ether (yield 91 per cent.) (Found: Na = 13.8 per cent.).

*Potassium Phthalimide* (with amyl alcohol as solvent).—The procedure was the same as that followed for the sodium derivative. No further yield was obtained from the filtrate (yield 97 per cent.) (Found: K = 21.2 per cent.).

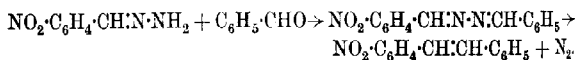
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[Received, September 22nd, 1922.]

## CCLXXXIV.—2:4-Dinitrobenzil.

By GERALD BISHOP and OSCAR LISLE BRADY.

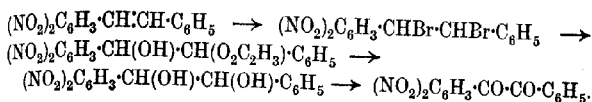
THE unsymmetrical benzils and their derivatives have not been studied to any great extent, although List (*Ber.*, 1893, **26**, 2451) has done some work on the oximes of *o*- and *p*-nitrobenzils. A certain amount of interest attaches to these compounds on account of the peculiarities often associated with unsymmetrical substances and the possibilities of isomerism among their derivatives; for example, on the usually accepted theories, there should exist four monoximes and four dioximes and a similar number of phenylhydrazones and semicarbazones. Possibly the difficulty of preparing these derivatives has militated against their investigation, the usual benzoin condensation not being available, as this must result in symmetrical compounds. The unsymmetrically substituted stilbenes seemed to be convenient starting materials, and the ease with which the unsymmetrical di- and tri-nitrostilbenes could be prepared by the condensation of di- and tri-nitrotoluenes with benzaldehyde led to the choice of these compounds for a preliminary investigation. Another method of preparation of stilbenes was investigated, but without satisfactory results. It is stated (Curtius and Jay, *J. pr. Chem.*, 1889, [ii], **39**, 45) that the azines on distillation lose nitrogen to give stilbenes,  $\text{CHR:N:N:CHR} \rightarrow \text{CHR:CHR} + \text{N}_2$ . This reaction takes place, but not so readily as one is given to understand; *p*-nitrobenzylideneazine on distillation in a vacuum is converted into 4:4'-dinitrostilbene, but when anisylideneazine is heated even under atmospheric pressure, much of the compound distils unchanged. This method would give symmetrical compounds, but it was hoped that the unsymmetrical azine could be obtained by condensing, for example, *m*-nitrobenzylidenehydrazine with benzaldehyde, and that the decomposition of these substances would yield the stilbene.



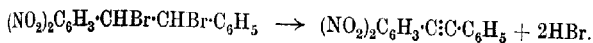
It was found, however, that treatment of the hydrazine with another aldehyde resulted in a mixture of the two symmetrical azines.

The conversion of the stilbene into the benzil depends, in the first instance, on the formation of the dibromo-compound. A number of poly-nitrostilbenes were investigated, and it was found that addition of bromine took place but very slowly if more than two nitro-groups were present in one ring; the 2:4-dinitrostilbene

obtained by the condensation of 2:4-dinitrotoluene and benzaldehyde in the presence of piperidine was therefore chosen. The subsequent conversion of this compound into 2:4-dinitrobenzil may be summarised by the following reactions:

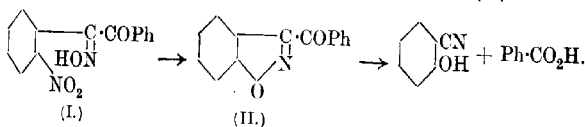


These call for no special comment beyond the fact that the replacement of bromine can be effected only by means of silver acetate; alcoholic potassium acetate results in an almost quantitative regeneration of the original stilbene, not, as might be expected, the acetylene derivative.

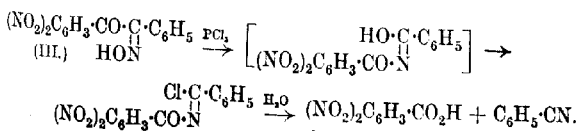


Forst and Zincke (*Annalen*, 1876, **182**, 262) found that this reagent converted stilbene dibromide into stilbene and  $\omega$ -bromostilbene. The position of the acetyl group in 2:4-dinitrohydrobenzoin acetate has not been proved, but it is reasonable to expect that it would take up the position more remote from the acidic dinitrophenyl group.

So far, only two of the four possible monoximes have been obtained;  $\alpha$ -2:4-dinitrobenzilmonoxime, formed by the action of hydroxylamine hydrochloride on the ketone, does not possess the same configuration that List (*loc. cit.*) found for the oxime of  $\alpha$ -nitrobenzil obtained in a similar manner. He assigns to his compound the structure (I) owing to its decomposition by alkalis into salicylic and benzoic acids through the indoxazen (II):

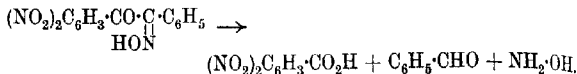


$\alpha$ -2:4-Dinitrobenzilmonoxime has the other carbonyl group oximated, and must have the structure (III), as the Beckmann transformation results in the production of benzonitrile and 2:4-dinitrobenzoic acid:

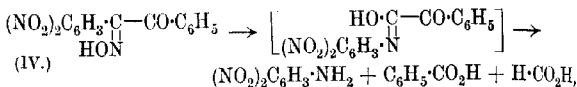




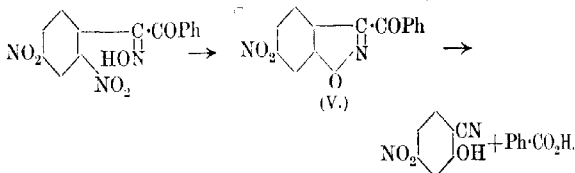
With alkali, the  $\alpha$ -monoxime is decomposed with the production of benzaldehyde and dinitrobenzoic acid:



$\beta$ -2:4-Dinitrobenzildioxime was prepared by the action of free hydroxylamine on an ice-cooled solution of the ketone, and this has a structure (IV) analogous to that of the oxime of List. The Beckmann transformation results in this case in the production of benzoic acid and dinitroaniline,



whilst the action of alkalis, even in the cold, is very rapid, giving benzoic acid and 4-nitrosalicylonitrile, the indoxazen (V) being very unstable and impossible to isolate.



So far, only one monophenylhydrazone and one semicarbazone have been prepared, but the configuration of these compounds has not yet been determined.

#### EXPERIMENTAL.

**2:4-Dinitrostilbene.**—Two methods have been described for the condensation of di- and tri-nitrotoluenes with aromatic aldehydes to give stilbene derivatives. Thiele and Escales (*Ber.*, 1901, **34**, 2843) prepared 2:4-dinitrostilbene by heating 2:4-dinitrotoluene with benzaldehyde in the presence of a few drops of piperidine for a short time at 160–170° and then for two hours at 130–140°. Pfeiffer and Monath (*Ber.*, 1906, **39**, 1306) prepared 2:4:6-trinitrostilbene and 2:6-dinitrostilbene in a somewhat similar manner. Later, Ullmann and Gschwind (*Ber.*, 1908, **41**, 2296) prepared 2:4:6-trinitrostilbene and 2:4:6:4'-tetranitrostilbene by condensing 2:4:6-trinitrotoluene with benzaldehyde and *p*-nitrobenzaldehyde in alcoholic solution in the presence of piperidine. These methods are not entirely satisfactory, especially in the case of the trinitro-compound, which, in the absence of a solvent, is

very liable to inflammation owing to the vigour of the reaction. Better results have been obtained by the use of benzene as a solvent, which moderates the reaction and avoids the formation of complex compounds of the nitrotoluenes with the piperidine and alcohol.

A mixture of 180 grams of 2:4-dinitrotoluene and 100 grams of benzaldehyde was dissolved in 70 c.c. of benzene, 1 c.c. of piperidine added, and the solution boiled on the water-bath under reflux for twelve hours, an additional 1 c.c. of piperidine being added at the end of six hours. The benzene was then evaporated and the dark brown, crystalline mass washed with a mixture of equal volumes of benzene and light petroleum. The residue was dried and crystallised from glacial acetic acid, when a 60 per cent. yield of pure product was obtained.

**2:4:6-Trinitrostilbene.**—A mixture of 20 grams of 2:4:6-trinitrotoluene and 9.6 grams of benzaldehyde was dissolved in 150 c.c. of benzene, a solution of 1.5 c.c. of piperidine in 10 c.c. of benzene added with thorough shaking, and the mixture heated under reflux on the water-bath for three hours. Alcohol (200 c.c.) was then added to the hot solution, and, on cooling and scratching, the trinitrostilbene separated in yellow crystals, which, after washing with cold alcohol, were practically pure, but may be crystallised from alcohol. Yield 80 per cent.

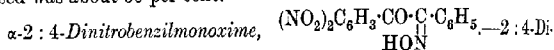
**2:4:6:2'- and 2:4:6:3'-Tetranitrostilbenes.**—To a benzene solution of 15 grams of 2:4:6-trinitrotoluene and 10 grams of *o*- or *m*-nitrobenzaldehyde, 1 c.c. of piperidine in 20 c.c. of benzene was added and the mixture heated under reflux on the water-bath for an hour. The mixture was then cooled and the tetranitrostilbene which crystallised out separated. 2:4:6:2'-Tetranitrostilbene crystallises from alcohol in glistening, light brown needles melting at 181° (Found: N = 15.5.  $C_{14}H_8O_8N_4$  requires N = 15.5 per cent.). 2:4:6:3'-Tetranitrostilbene crystallises from boiling benzene, to which a little acetone has been added to increase the solvent action, in lemon-yellow leaflets melting at 159° (Found: N = 15.3.  $C_{14}H_8O_8N_4$  requires N = 15.5 per cent.).

**Monacetyl-2:4-dinitrohydrobenzoin.**—The 2:4-dinitrostilbene was brominated in the way described by Thiele and Escales (*loc. cit.*) and the resulting 2:4-dinitrodibromostilbene boiled with silver acetate in glacial acetic acid solution until no more silver bromide was precipitated (compare Forst and Zincke, *loc. cit.*, who obtained a mono- and a di-acetylhydrobenzoin from stilbene dibromide by this method). On pouring into water, a yellow, resinous mass separated which became partly crystalline after some hours. A portion was crystallised from glacial acetic acid,

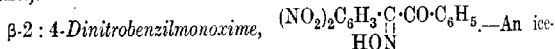
when the monoacetyl-2:4-dinitrohydrobenzoin separated in large, irregular, lemon-yellow crystals melting at  $182^{\circ}$  (Found: Ac = 12.7,  $C_{16}H_{14}O_7N_2$  requires Ac = 12.4 per cent.). Decomposition of the dibromodinitrostilbene with sodium or potassium acetate under various conditions resulted in its conversion into the original stilbene.

**2:4-Dinitrohydrobenzoin.**—The crude acetyl compound obtained above was hydrolysed by boiling under reflux for an hour with alcohol containing 20 per cent. of sulphuric acid. On pouring the solution into water, a soft, wax-like substance was precipitated which, by crystallisation from alcohol, gave the 2:4-dinitrohydrobenzoin as a white, crystalline powder melting at  $148^{\circ}$  (Found: N = 9.6.  $C_{14}H_{12}O_6N_2$  requires N = 9.2 per cent.).

**2:4-Dinitrobenzil.**—The above dinitrohydrobenzoin was heated on the water-bath with four times its weight of nitric acid ( $d$  1.4) until brown fumes were no longer evolved (about six hours). On pouring into water, a yellow, wax-like solid was obtained which, on washing with a little ether, gave the dinitrobenzil in a crystalline form. This was purified by crystallisation first from glacial acetic acid and then from alcohol, when the 2:4-dinitrobenzil was obtained in canary-yellow, rectangular plates melting at  $105^{\circ}$  (Found: N = 9.4.  $C_{14}H_8O_6N_2$  requires N = 9.3 per cent.). The total yield of 2:4-dinitrobenzil calculated on the dinitrostilbene used was about 30 per cent.



nitrobenzil in alcoholic solution was heated with hydroxylamine hydrochloride (3 mols.) on the water-bath for two hours. The mixture was poured into water and the precipitated oxime crystallised from alcohol, when it was obtained in pearly leaflets melting at  $181^{\circ}$  (Found: N = 13.6.  $C_{14}H_9O_6N_3$  requires N = 13.3 per cent.).



cooled solution of 2:4-dinitrobenzil in alcohol was shaken with excess of an alcoholic solution of free hydroxylamine, prepared by decomposing an alcoholic solution of the hydrochloride with the calculated quantity of sodium dissolved in alcohol. After a few minutes, a white precipitate appeared which at the end of an hour was collected, dried, and crystallised from benzene and light petroleum. The oxime was thus obtained as a white, microcrystalline powder melting at  $159^{\circ}$  (Found: N = 13.1.  $C_{14}H_9O_6N_3$  requires N = 13.3 per cent.).

*Determination of the Configuration of  $\alpha$ - and  $\beta$ -2:4-Dinitrobenzil-*

*monoxime*.— $\alpha$ -2:4-Dinitrobenzilmonoxime was dissolved in dry ether, cooled in ice, and the calculated quantity of phosphorus pentachloride added. After about an hour, a white substance began to separate and after five hours this was collected, washed with a little alcohol and then with water, dried, and crystallised from benzene and light petroleum. The chloro-compound formed a white, crystalline powder which slowly decomposed on heating (Found: N = 12.9.  $C_{14}H_8O_5N_3Cl$  requires N = 12.6 per cent.). Leaving in contact with moist ether resulted in the decomposition of this substance into benzonitrile and dinitrobenzoic acid, a result which can be brought about more readily by shaking an ethereal suspension with dilute sodium hydroxide solution. The ether layer on evaporation yielded benzonitrile, which was identified by its odour and by hydrolysis to benzoic acid and ammonia, whilst the alkaline layer, on acidification, yielded 2:4-dinitrobenzoic acid. When  $\beta$ -2:4-dinitrobenzilmonoxime was treated in a similar manner, the intermediate compound was not isolated. The ethereal solution was therefore shaken with sodium hydroxide solution; benzoic acid was separated from the alkaline layer, and the ether on evaporation gave an oil with a carbylamine-like odour which on hydrolysis gave 2:4-dinitroaniline.

*Action on Alkalis of  $\alpha$ - and  $\beta$ -2:4-Dinitrobenzilmonoxime*.—The  $\alpha$ -oxime, on heating on the water-bath with 2N-sodium hydroxide, was decomposed, a strong odour of benzaldehyde being observed; the benzaldehyde was distilled in steam and identified by the formation of the semicarbazone. The alkaline liquor on acidification gave a brown, amorphous precipitate which deflagrated on heating and appears to be the usual product of the action of warm alkalis on dinitrobenzoic acid.

The  $\beta$ -oxime is much more readily acted upon and treatment with cold 2N-sodium hydroxide resulted in elimination of nitrous acid and decomposition of the resulting indoxazen into 4-nitrosalicylonitrile and benzoic acid. The oxime was treated with cold 2N-sodium hydroxide and after leaving for a few minutes the solution was saturated with carbon dioxide and extracted with ether. The alkaline layer, on acidification and extraction with ether, yielded benzoic acid; the ethereal extract on evaporation gave 4-nitrosalicylonitrile, which, after crystallisation from alcohol, melted at  $169^\circ$  (compare Borsche and Oppenheimer, *Annalen*, 1912, **390**, 10) and was identified by hydrolysis to 4-nitrosalicylic acid and comparison with another specimen of that compound.

*2:4-Dinitrobenzilmonophenylhydrazone*.—An alcoholic solution of 2:4-dinitrobenzil was heated on the water-bath for an hour with phenylhydrazine (3 mols.). The mixture was poured into water

and the precipitated phenylhydrazone crystallised from alcohol, when it separated in orange-red needles melting at  $210^{\circ}$  (Found:  $N = 14.5$ .  $C_{20}H_{14}O_5N_4$  requires  $N = 14.3$  per cent.).

2 : 4-Dinitrobenzilmonosemicarbazone.—An aqueous alcoholic solution of 2 : 4-dinitrobenzil was warmed on the water-bath for half an hour with excess of semicarbazide hydrochloride and potassium acetate. The solution was poured into water and the precipitate crystallised from alcohol, when the semicarbazone was obtained as a white, crystalline powder melting at  $215^{\circ}$  (Found:  $N = 19.5$ .  $C_{15}H_{11}O_6N_5$  requires  $N = 19.5$  per cent.).

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### CCLXXXV.—*Mutarotation and Pseudo-mutarotation of Glucosamine and its Derivatives.*

By JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL.

In a previous communication (Irvine and Hynd, T., 1913, **403**, 4), a description was given of synthetical aminoglucosides derived from *d*-glucosamine, and attention was directed to the curious optical behaviour of the compound then termed "triacetyl  $\alpha$ -aminohelcin hydrobromide." It was stated that the glucoside salt showed in methyl alcohol an initial specific rotation of  $+200.1^{\circ}$  and that this value steadily diminished to  $+43.5^{\circ}$ , where it remained constant. As glucosides do not display mutarotation under ordinary conditions, the suggestion was put forward that this change in activity might be due to interaction between the aldehyde group of the glucoside and the solvent alcohol. The name "*pseudo-mutarotation*" was accordingly applied to the phenomenon, as it involved a reaction not readily reversible.

An opportunity having arisen to resume our studies of glucosamine derivatives, we have examined this case of pseudo-mutarotation in greater detail and have included also a reinvestigation of the normal mutarotation displayed by glucosamine hydrochloride. As the observations made on the salt of the amino-sugar have an indirect bearing on its relationship to either glucose or mannose, they may be discussed in the first instance.

In describing our new results it is necessary to refer to earlier work on the subject, as otherwise confusion may arise owing to the nomenclature formerly applied to mutarotatory isomerides. Tanret (*Bull. Soc. chim.*, 1897, [iii], **17**, 802) recorded the existence of two modifications of glucosamine hydrochloride which he diff-

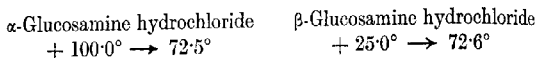
entiated by the prefixes  $\alpha$  and  $\beta$ . The former type showed in aqueous solution an initial specific rotation of  $+100^\circ$ , which diminished to the constant value  $+72.5^\circ$ . The variety of glucosamine hydrochloride then existing in solution was isolated by precipitation with alcohol, and was termed the  $\beta$ -form by Tanret. In the light of current views, this nomenclature is inexact, as, although the name " $\alpha$ -glucosamine hydrochloride" may justifiably be applied to the form showing downward mutarotation, the expression  $\beta$  should be reserved for the isomeride displaying the converse optical change. Tanret's " $\beta$ -glucosamine hydrochloride" is obviously an equilibrium mixture of  $\alpha$ - and  $\beta$ -isomerides, and it would appear that hitherto no workers have obtained a form of the amino-sugar showing upward mutarotation, although, from analogy with other reducing sugars, such a form should exist. The isolation of authentic  $\beta$ -glucosamine hydrochloride is, in fact, a matter of some importance, as it bears on the question of whether glucosamine possesses the glucose or mannose configuration. It has been established by Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66; 1910, **32**, 889) that definite numerical relationships exist between the molecular rotations displayed by  $\alpha$ - and  $\beta$ -forms of most aldose sugars, the difference of the two values usually lying between the limits 16,500 and 18,500. Now, accepting Tanret's figures for the varieties of glucosamine hydrochloride he describes, the molecular rotation difference is 5950. According to this result, glucosamine is comparable, not with glucose, but with mannose, which shows divergence in optical behaviour from the normal aldoses. It is clear, therefore, that failure to isolate a variety of glucosamine hydrochloride showing upward mutarotation would immediately place glucosamine in the same category as mannose. On the other hand, if a form of glucosamine hydrochloride were obtained which displayed on solution an increase of rotation in the dextro-sense, the optical values might conform to Hudson's generalisations and thus bring glucosamine into line with glucose.

It has now been definitely established that Tanret's " $\beta$ -glucosamine hydrochloride" is not a pure optical variety, but a mixture of two forms showing widely divergent specific rotations. As described in the experimental part, this mixture was separated approximately by dissolving in water and pouring into alcohol, the  $\alpha$ -form being thus precipitated and the more soluble  $\beta$ -variety retained in solution. On the addition of ether, the  $\beta$ -form was precipitated. This showed extensive upward mutarotation in the dextro-sense when dissolved in water, and by systematic fractional precipitation a pure stereochemical form of  $\beta$ -glucosamine hydrochloride was finally obtained. A comparison of the reverse optical

changes shown by the two varieties of glucosamine hydrochloride is given below, only characteristic figures being quoted:

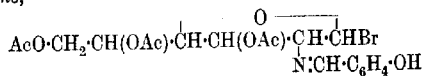
Time of contact of solvent and solute.	$\alpha$ -Form. $c = 1.3512$ .	$\beta$ -Form. $c = 1.369$ .
3 minutes	+ 97.9°	+ 32.6°
14 "	+ 93.9	+ 38.3
45 "	+ 84.7	+ 51.1
20 hours	+ 72.5 constant	+ 72.6 constant

When the complete polarimetric records are plotted graphically the curves are perfectly normal and conform closely to those obtained with unsubstituted mutarotatory sugars. Extrapolation of the results gives the following initial values, which may be assigned to the two forms:



On this basis, the molecular rotation difference is thus 16,160, and as in the case of glucose the corresponding constant is of the order 16,900, it follows that the divergence is less than 0.5 per cent.\* Glucosamine therefore conforms to Hudson's rule in the same manner as glucose, and is sharply differentiated in this respect from mannose. The result may be cited as additional evidence in favour of the glucose configuration for the amino-sugar.

Turning to the question of the pseudo-mutarotation formerly ascribed to triacetyl  $\alpha$ -aminohelicin hydrobromide, we have ascertained that the tentative explanation put forward to account for this change is incorrect. When triacetyl bromoglucosamine hydrobromide reacts with salicylaldehyde, glucoside-formation takes place only to a limited extent, the main reaction being condensation between the aldehydic group and the amino-group. The product is therefore not a true glucoside but *salicylidene triacetyl bromoglucosamine*,



The compound melts at 118°, and although unusual difficulties were encountered in obtaining consistent analytical figures, there can be little doubt from a study of its reactions that the formula given

\* It may be stated that Irvine and Hogg (T., 1914, 105, 1386), who determined the molecular rotation difference for the  $\alpha$ - and  $\beta$ -forms of monomethyl glucose, obtained a result practically identical with that now established for glucosamine (16,141 compared with 16,160).

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above represents the correct constitution.\* If the bromine atom is attached to carbon and is not present in the form of an additive molecule of hydrogen bromide, as was originally supposed, the compound should react with any hydroxy-substance to give the corresponding glucoside. Such changes would naturally result in alterations in rotatory power, but, on the other hand, the activity should remain constant in non-hydroxylic solvents. This view has been confirmed.

Solvent.	Initial specific rotation.	Final specific rotation.	Solvent.	Initial specific rotation.
Methyl alcohol	+241.9°	+48.4°	Salicylaldehyde	+193.2° constant
Ethyl "	197.7	51.1	Chloroform	199.2 constant
Propyl "	182.1	49.9	Acetone	195.2 constant
isoButyl "	182.2	55.6	Ethyl acetate	177.7 constant
Amyl "	169.5	54.5		
Benzyl "	218.4	32.4		
Allyl "	192.8	75.6		
Methyl malate	336.8	251.9		

With the exception of the one solvent which contained a phenolic group, all the hydroxy-compounds reacted with the solute, whilst non-hydroxy-compounds were without effect. The general reactions involved in the pseudo-mutarotation were ascertained by examination of methyl alcoholic solutions. On isolating the product after six days, the chief constituent was found to be 2-salicylidene-3:5:6-triacetyl-1-methyl glucosamine (that is, salicylidene triacetyl methylglucosamine). At the same time, free hydrogen bromide was formed, and this gradually removed the salicylidene residue, so that when the pseudo-mutarotation extended over several weeks the final product formed was 3:5:6-triacetyl-1-methyl glucosamine. These results are in themselves quite conclusive, and were supported by the reaction between triacetyl bromoglucosamine and *o*-methoxybenzaldehyde. Although no hydroxyl group was present in this case, the aldehyde readily entered into condensation, giving 1-bromo-2-*o*-methoxybenzyldene-3:5:6-triacetylglucosamine. This compound likewise exhibited pseudo-mutarotation when dissolved in alcohols, giving in the case of methyl alcohol triacetylmethylglucosamine as the final product.

\* The analytical values quoted by Irvine and Hynd (*loc. cit.*) on which the above compound was regarded as the hydrobromide of an acetylated aminohelicin, have been confirmed on more than one occasion, but the agreement with the calculated value for carbon is fortuitous. In the case of the hydrogen, bromine, and nitrogen estimations, the calculated composition is practically identical for the helicin derivative or the salicylidene compound, and thus the analysis was not discriminative.



## EXPERIMENTAL.

*Isolation of  $\beta$ -Glucosamine Hydrochloride.*

The glucosamine hydrochloride employed was prepared as formerly described (Irvine, McNicoll, and Hynd, T., 1911, 99, 256) by the hydrolysis of chitin isolated from lobster shells. As the recrystallised material consisted largely of the  $\alpha$ -form, it was dissolved in water and after heating the solution on a water-bath to promote equilibrium with the  $\beta$ -variety it was poured into a large excess of absolute alcohol. The precipitated salt was then filtered and dried.

*Method I.*—Fifteen grams of the dry solid were finely powdered and shaken vigorously in the machine for ten minutes with 250 c.c. of cold absolute alcohol. The undissolved salt was removed and 500 c.c. of benzene were added to the filtrate, which was again shaken for twenty minutes. During this treatment a small crop (1.8 grams) of  $\beta$ -glucosamine hydrochloride gradually separated. After drying, this gave correct analytical figures and showed the upward mutarotation  $+35.0^\circ \rightarrow +71.7^\circ$ . The method gives the  $\beta$ -compound directly in a pure optical condition, but as the yield is small the process is not so advantageous as the alternative now described.

*Method II.*—Fifty grams of glucosamine hydrochloride were dissolved in 125 c.c. of water, the solution being heated on a water-bath for twenty-five minutes and kept over-night. Thereafter the liquid was poured into 375 c.c. of absolute alcohol and after shaking for ten minutes the precipitated salt (fraction A) was removed and the filtrate poured into a mixture of 250 c.c. of absolute alcohol and 250 c.c. of ether. The liquid was again shaken for ten minutes and a second fraction (B) collected, a third fraction (C) being obtained on pouring the filtrate into a mixture of 125 c.c. of absolute alcohol and 500 c.c. of ether. The weights and optical behaviour of these fractions are shown below :

(A)	27.75 grams,	$[\alpha]_D + 87.0^\circ \rightarrow + 72.7^\circ$	in 24 hours,	$c = 1$
(B)	4.2     ,,	$[\alpha]_D + 57.6^\circ \rightarrow + 72.3^\circ$	,,     ,,	$c = 1$
(C)	5.8     ,,	$[\alpha]_D + 32.6^\circ \rightarrow + 71.7^\circ$	,,     ,,	$c = 1$

In the course of repeated preparations glucosamine hydrochloride corresponding with fraction B was accumulated and subjected to the same process of fractional precipitation by the use of alcohol and ether. In this way, additional quantities of fraction C were obtained. The combined material constituting fraction C was again precipitated fractionally, but as no alteration in the initial specific rotation was obtained, it was evident that the above process

gives the compound in an optically pure state. Beyond what is stated in the introduction, no details need be given of the downward mutarotation shown by  $\alpha$ -glucosamine hydrochloride, as this form of the compound was prepared in the usual manner by crystallisation from a hot concentrated aqueous solution.

Comparative experiments showed that the  $\beta$ -form reacted more readily with acetyl bromide than the  $\alpha$ -isomeride, giving improved yields of triacetyl bromoglucosamine.

*Condensation of Salicylaldehyde with Triacetyl Bromoglucosamine.*

It has been frequently emphasised by previous workers that in all reactions involving the use of triacetyl bromoglucosamine moisture must be rigidly excluded. This precaution is justified and was adhered to in the present work.

The above condensation was carried out on numerous occasions, but only one typical experiment need be quoted. 9.7 Grams of the recrystallised bromo-compound (1 mol.) were suspended in 30 c.c. of ether, and 1.6 c.c. of pyridine (1 mol.) together with 12 c.c. of salicylaldehyde (3 mols.) were then added. The mixture was shaken for one hour and, after filtration, was precipitated by the addition of light petroleum, the product separating as a mass of brilliant yellow needles. Yield 6.7 grams. Purification was effected by solution in ether and precipitation with light petroleum and, after four crystallisations by this method, the compound was pure. Although the maximum melting point recorded was  $18^{\circ}$ , average specimens show  $109-110^{\circ}$ .

It was not found possible to obtain consistent analytical results by the combustion process, the carbon values in particular showing considerable variation. The nitrogen content is too small to afford trustworthy evidence as to composition, but, on the other hand, bromine estimations gave concordant results. Although individual combustions varied greatly, the analytical figures now quoted represent the mean of five analyses carried out on independent preparations and indicate the composition (Found: C = 8.40; H = 4.83; Br = 16.74.  $C_{19}H_{22}O_8NBr$  requires C = 48.30; H = 4.66; Br = 16.92 per cent.). The analyses, together with the actions of the compound, show it to be 1-bromo-2-salicylidene-3:5:6-triacetyl glucosamine (that is, salicylidene triacetyl bromoglucosamine).

*Action of Methyl Alcohol on 1-Bromo-2-salicylidene-3:5:6-triacetyl Glucosamine.*

A 5 per cent. solution of the bromo-derivative in methyl alcohol was preserved for six days and the solvent then removed under

diminished pressure at the temperature of the room. A semi-crystalline syrup remained which, after repeated solution in methyl alcohol and precipitation with ether, yielded 1-methyl-3:5:6-triacetyl glucosamine hydrobromide (Irvine and Hynd, *loc. cit.*), which was identified by analysis and specific rotation. The mother-liquors gave a small quantity of a golden-yellow, crystalline solid which proved to be 2-salicylidene-3:5:6-triacetyl-1-methyl glucosamine [Found: OMe = 6.51.  $C_{19}H_{22}O_8N(OMe)$  requires OMe = 6.15 per cent.]. When the action of methyl alcohol on salicylidene triacetyl bromoglucosamine was prolonged for several weeks, a different result was naturally obtained. On removing the solvent as before and crystallising the residue by solution in a small quantity of methyl alcohol, followed by addition of ether, a white, crystalline solid was obtained. This melted and decomposed at 233–234° and showed  $[\alpha]_D + 21.7^\circ$  in methyl alcoholic solution. These constants together with the analytical results show the product to be 3:5:6-triacetyl 1-methyl glucosamine hydrobromide (that is triacetyl methylglucosamine hydrobromide).

No description need be given of the action of *o*-methoxybenzaldehyde on triacetyl bromoglucosamine or of the action of methyl alcohol on the product, as the methods employed were exactly similar to those described above. In this case also, the ultimate decomposition product proved to be triacetyl methylglucosamine hydrobromide [Found: OMe = 8.1; Br = 19.72;  $[\alpha]_D = + 22.9^\circ$ ; decomposition point 232°.  $C_{12}H_{18}O_7(OMe), HBr$  requires OMe = 7.75; Br = 19.97 per cent.;  $[\alpha]_D = + 20.3^\circ$ ; decomposition point 230–233°].

The authors desire to express their thanks to Alexander D. Muir (Carnegie Scholar) for much valuable assistance.

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### CCLXXXVI.—*Salicylidene Derivatives of d-Glucosamine.*

By JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL.

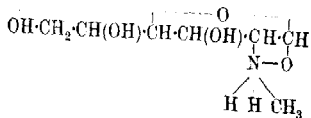
IN the preceding paper it is shown that salicylaldehyde reacts readily with the amino-group of triacetyl bromoglucosamine to give a characteristic salicylidene derivative. The highly reactive bromine atom present in the glucosamine chain takes no part

this condensation, and the reasonable conclusion may be drawn that any substituted glucosamine, in the form of the free base, will react in a similar manner. This expectation has been realised and typical salicylidene derivatives of glucosamine are now described. As these compounds are readily formed, crystallise with ease, and possess convenient solubilities, they are likely to prove of service in developing the chemistry of the amino-sugar.

The method of preparation consists in dissolving the glucosamine salt in water, liberating the free base by the addition of alkali, and then agitating the solution with salicylaldehyde. The salicylaldene derivative generally separates directly in the crystalline condition. The properties of five typical examples may now be summarized, as their study has opened out some interesting theoretical considerations.

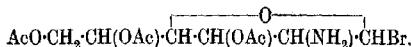
	Colour.	M. p.	[ $\alpha$ ] <sub>D</sub> in methyl alcohol.	Yield per cent.
2-Salicylidene glucosamine	Canary-yellow	153.5°	+11.0°	99
2-Salicylidene-1-methyl glucosamine	Deep yellow	120	+2.2	26
2-Salicylidene-3:5:6-triacetyl-1-methyl glucosamine	Pale yellow	151	+75.7	80
2-Salicylidene-3:5:6-triacetyl-1-ethyl glucosamine	Pale yellow	135	+40.7	88
1-Bromo-2-salicylidene-3:5:6-triacetyl glucosamine	Canary-yellow	118	+241.9	65-70

It is significant that with one exception the formation of these leydene compounds proceeded with unusual smoothness. The exception is presented by methylglucosamine, which reacted with leylaldehyde only with difficulty, giving a 26 per cent. yield of the product. This comparative failure to participate in the normal reaction cannot be due to the presence of the methyl group in view of the results obtained with the acetylated glucosides, nor is it attributable to the absence of acetyl groups, as free glucosamine reacted with extreme ease. The abnormal behaviour of methylglucosamine is thus in agreement with the cyclic formula previously suggested for this compound.

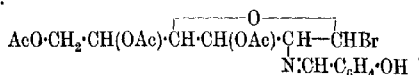


the composition of triacetyl bromoglucosamine, which is starting point in synthetical work in this series, does not fit of a formula of the above type and the compound must

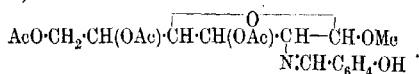
therefore possess the normal structure characteristic of reducing sugars:



It follows that the corresponding salicylidene derivative in which the reactive bromine atom is retained must also be an open chain structure:



When this compound reacts with methyl alcohol to give a "methylglucoside" there seems no reason why profound structural alteration should accompany the change, and the compound formed may be termed 2-salicylidene-3:5:6-triacetyl-1-methylglucosamine,



The reactions sketched above have been carried out, and the final product proved to be identical with that obtained when salicylaldehyde was condensed with triacetyl methylglucosamine. In other words, no isomerism is involved if the order of introducing the methyl group and the salicylidene residue is varied. The argument leads to the conclusion that triacetyl methylglucosamine is not constituted on the betaine model, but that a change to this type occurs when the acetyl groups are eliminated. It is, of course, possible that triacetyl methylglucosamine may exist in both forms, and in the experimental part a levorotatory isomeride of this compound is described. This new variety is being further investigated, but the combined results submitted evidently afford strong support to the view formerly expressed that in methylglucosamine the alkyl group is directly attached to the nitrogen atom.

#### EXPERIMENTAL.

##### *Salicylidene Glucosamine.*

Ten grams of glucosamine hydrochloride (1 mol.) and 6.3 grams of sodium bicarbonate ( $1\frac{1}{2}$  mols.) were dissolved in 100 c.c. of water, and 6.3 c.c. of salicylaldehyde (1 mol.) added. The mixture was stirred vigorously at the temperature of the room, and in thirty minutes the separation of crystals commenced. Stirring was continued for three and a half hours, when the product was filtered, washed with cold water, and dried in a vacuum. The yield was 13 grams (99 per cent.). After recrystallisation from

methyl alcohol, the compound melted sharply at  $183.5^{\circ}$  (Found: C = 54.92; H = 6.18.  $C_{13}H_{17}O_5N$  requires C = 55.09; H = 6.05 per cent.).

Salicylidene glucosamine crystallises in bright yellow needles, insoluble in chloroform, but readily dissolved by hot methyl or ethyl alcohol. The compound was easily hydrolysed by dilute acids, giving salicylaldehyde and the corresponding salt of glucosamine.

*2-Salicylidene-1-methyl Glucosamine* (Salicylidene Methylglucosamine).

7.5 Grams of recrystallised methylglucosamine hydrochloride were dissolved in 100 c.c. of water containing 3.75 grams of sodium bicarbonate and 3.2 c.c. of salicylaldehyde. The liquid, which was stirred for two hours, soon acquired a yellow colour and deposited a clear syrup, which adhered to the sides of the vessel. Excess of chloroform was then added and the mixture was shaken repeatedly with this solvent, and after drying the extract over magnesium sulphate, it was evaporated to a small bulk. On the addition of light petroleum, the product separated in a semi-crystalline condition. Purification was effected by again dissolving in chloroform and precipitating in the manner described above, salicylidene methylglucosamine being thus obtained in bright yellow needles melting at  $120^{\circ}$ . The yield from the experiment just described was 1.7 grams (26 per cent.), and this was not improved in subsequent preparations [Found: C = 56.33; H = 6.41; OMe = 9.63.  $C_{13}H_{16}O_5N(OMe)$  requires C = 56.56; H = 6.39; OMe = 10.47 per cent.]. Salicylidene methylglucosamine is readily hydrolysed by acids to regenerate methylglucosamine. On the other hand, the action of nitrous acid involves the removal of the salicylidene residue followed by the elimination of the amino- and glucosidic groups.

*2-Salicylidene-3:5:6-triacetyl-1-methyl Glucosamine* (Salicylidene Triacetyl Methylglucosamine).

Two distinct methods were employed in the preparation of this compound and their significance is referred to in the introduction.

*Method I.*—A solution of 5.3 grams of 1-bromo-2-salicylidene-3:5:6-triacetyl glucosamine in 30 c.c. of methyl alcohol was mixed with 3.2 grams of morphine, dissolved in 60 c.c. of the same solvent. When the mixture was kept at the temperature of the room for seven days, morphine hydrobromide gradually separated. The filtrate, on evaporation under diminished pressure, gave a solid residue, which was recrystallised from alcohol. Yield 50 per cent.

*Method II.*—8.2 Grams of recrystallised triacetyl bromoglucosamine hydrobromide were dissolved in 100 c.c. of methyl alcohol containing 1.65 c.c. of pyridine. The solution was set aside for twenty hours, filtered, and concentrated to a small bulk at 25°/90 mm. Thereafter a solution of 3.5 grams of sodium bicarbonate in 40 c.c. of water was added together with 1.95 c.c. of salicylaldehyde. Vigorous stirring occasioned the separation of the crystalline product, which, after thirty minutes, was filtered and washed with cold water. One recrystallisation from alcohol gave a pure product melting at 151–152°. Yield 80 per cent. (Found: C = 56.93; H = 6.25; OMe = 8.2.  $C_{20}H_{25}O_4N$  requires C = 56.71; H = 5.95; OMe = 7.3 per cent.). The salicylidene derivative crystallises in pale yellow, prismatic needles readily soluble in hot alcohol;  $[\alpha]_D$  in methyl alcohol + 75.7° for  $c = 1$ . The three acetyl groups in the compound are remarkably stable, but were quantitatively removed by distillation with 15 per cent. sulphuric acid. After four hours' treatment with absolute alcohol saturated with ammonia at 0°, no acetamide was formed, and 70 per cent. of the original material was recovered unaltered (Fischer, *Ber.*, 1914, **47**, 218).

*Action of Nitrous Acid.*—When salicylidene triacetyl methylglucosamine was suspended in water and an aqueous solution of nitrous acid (prepared from silver nitrite) gradually added with vigorous stirring, no visible reaction ensued until the temperature was raised to 50°. The solid then passed into solution with copious evolution of nitrogen and liberation of salicylaldehyde. On neutralising the solution with barium carbonate, a quantity of salicylidene triacetyl methylglucosamine was regenerated and was precipitated in the crystalline state. The filtrate was evaporated to dryness under diminished pressure and extracted with boiling alcohol. This extract contained a glucosidic syrup, which was deacetylated by boiling with acidified methyl alcohol. After neutralisation with silver carbonate and removal of the solvent, a non-crystalline syrup remained which behaved as a glucoside towards Fehling's solution, but could not be identified either as methylglucoside or methylmannoside.

### 2. Salicylidene-3 : 5 : 6-triacetyl-1-ethyl Glucosamine (Salicylidene Triacetyl Ethylglucosamine).

Starting from triacetyl ethylglucosamine, the usual method of preparation was employed and gave an 88 per cent. yield of the above product [Found: C = 57.51; H = 6.39; OEt = 10.14.  $C_{20}H_{21}O_8N(OEt)$  requires C = 57.63; H = 6.18; OEt = 10.29 per cent.]. In every respect the compound resembled the corre-

sponding methyl derivative, m. p.  $131^{\circ}$ ,  $[\alpha]_D$  in methyl alcohol  $+40.7^{\circ}$  for  $c = 1$ .

3:5:6-Triacetyl-1-methyl Glucosamine (Triacetyl Methylglucosamine).

For reasons given in the introduction, the preparation of this compound from triacetyl bromoglucosamine was repeated.

(a) *Using pyridine*: The method adopted was identical with that described by Irvine, McNicoll, and Hynd (*loc. cit.*), and the properties previously assigned to the product were confirmed. The specific rotation in methyl alcohol was, however, slightly higher ( $+23.3^{\circ}$  in place of  $+20^{\circ}$ ).

(b) *Using morphine*: This preparation was conducted according to the variation recommended by Irvine and Hynd (*T.*, 1912, **101**, 1137) and the crude product was crystallised repeatedly by solution in methyl alcohol and the addition of ether. The finely divided solid was then extracted with methyl alcohol in the cold, the filtrate being concentrated and precipitated with ether. Repetition of these processes gave a small, crystalline crop which decomposed at  $201-202^{\circ}$  and showed  $[\alpha]_D$  in methyl alcohol  $-14.6^{\circ}$  for  $c = 1.8656$  [Found: C = 39.00; H = 5.79; OMe = 8.0.  $C_{12}H_{18}O_7N(OMe).HBr$  requires C = 38.99; H = 5.55; OMe = 7.75 per cent.]. No morphine aminoglucoside was present, and the compound is thus a new stereoisomeric form of triacetyl methylglucosamine hydrobromide.

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CCLXXXVII.—*The Mobility of Symmetrical Triad Systems. Part I. The Conditions Relating to Systems Terminated by Phenyl Groups.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED FIGGOTT.

It is the purpose of this series of papers to examine comparatively the mobility of symmetrical tautomeric systems of the general formula  $[H]X \cdot Y \cdot X$ . Six systems fall within the purview of this subject:

- Group (i)  $\begin{cases} \text{(i) the carboxyl group, } [H]O \cdot \overset{!}{C} \cdot O \\ \text{(ii) the acinitro-group, } [H]O \cdot \overset{!}{N} \cdot O \end{cases}$



- Group (ii)  $\left\{ \begin{array}{l} \text{(iii) the diazoamino-system, } \cdot[\text{H}]\text{N}\cdot\text{N}\cdot \\ \text{(iv) the amidine system, } \cdot[\text{H}]\text{N}\cdot\text{C}\cdot\text{N}\cdot \\ \text{(v) the methylenemethylamine system, } \cdot[\text{H}]\text{C}(\text{N})\cdot\text{C}\cdot \\ \text{(vi) the three-carbon (propene) system, } \cdot[\text{H}]\text{C}\cdot\text{C}\cdot\text{C}\cdot \end{array} \right.$

With regard to the first two (group i), the circumstantial evidence as to the equivalent functions of the two oxygen atoms is of the strongest character, but only the last four systems (group ii) are capable of being investigated as regards their mobility by the methods illustrated in this paper. It is proposed to investigate the behaviour of these four systems when attached to different types of terminal group, the present paper being primarily concerned with the terminal phenyl group, and hence with the comparison of the following four substances :

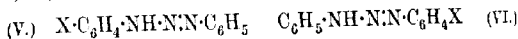


Some of the data necessary for this comparison are already on record and the remainder is given in the experimental portion of this paper.

The proof of the mobility of the three-nitrogen system present in diazoaminobenzene (I) rests on two types of evidence, both of which find their parallel in the experiments described hereunder :

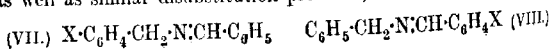
(A) Proof that only a single substitution product exists where two substances having formulæ (V) and (VI) might be expected (Griess, *Annalen*, 1866, **137**, 60; *Ber.*, 1874, **7**, 1619; and others).

(B) Proof that the single individual referred to under (A), on fission at the double bond (as by reduction or hydrolysis), gives four products, two derived from the two fragments of each of the hypothetical substances (V) and (VI) (Noelting and Binder, *Ber.*, 1887, **20**, 3095; and others).



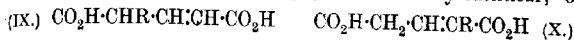
The same two types of evidence have been advanced in relation to diphenylformamidine (II) and its derivatives (Marekwald, *Annalen*, 1895, **285**, 348; von Pechmann, *Ber.*, 1897, **30**, 1783, and earlier; Wheeler and Johnson, *Ber.*, 1899, **32**, 35, and earlier).

In view of these facts, it was at first a matter for surprise to us on turning to the third of the four systems under comparison that both the above mobility tests (A and B) failed when applied to derivatives of benzyldenebenzylamine (III). Pairs of isomeric monosubstitution products of the general types (VII) and (VIII), as well as similar disubstitution products, not only were different

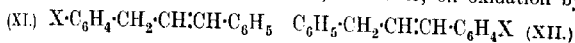


from one another, but also, apparently, were quite incapable of interconversion. Each individual, moreover, on fission, by acid hydrolysis, at the double bond gave two and not four resultants, the two being the aldehyde and amine by the interaction of which the substance in question was originally prepared (examples, pp. 2385, 2386).

The three-carbon system present in  $\alpha\gamma$ -diphenylpropene (IV) has a special interest in view of the close analogy between this substance and glutaconic acid, the three-carbon system of which is known to possess a high degree of mobility. The application to glutaconic acid of method (A) (above) was accomplished by Thole and Thorpe (T., 1911, 99, 2193), who proved that  $\alpha$ - and  $\gamma$ -alkyl derivatives, which, from the manner of their synthesis, would be expected to have formulæ such as (IX) and (X), were actually identical; on



the other hand, evidence of type (B) is to be found in the recent experiments of Feist, who, in several instances, obtained four products on fission by oxidation with ozone, two corresponding with each of the two static formulæ of the substance (*Annalen*, 1922, 428, 51, 71). The glutaconic acids, therefore, respond to both mobility tests, and it was fully expected that the  $\alpha\gamma$ -diphenylpropenes, in view of their close relationship with the glutaconic acids, would behave in an analogous manner. It was found, however, that the two phenyl groups in diphenylpropene are not equivalent, and that corresponding substitution products of types (XI) and (XII) show no tendency to undergo conversion one into the other (test A); each individual, moreover, on oxidation by



permanganate (test B) gives, not four, but two fission products corresponding with the particular static formula assigned to the substance (examples, pp. 2386, 2389).

From the above summary it will be evident that the molecular machinery necessary to produce a condition of tautomerism cannot consist solely of the formal "tautomeric system" and a potentially mobile hydrogen atom in the correct position. Some activating factor or condition must also be present, for only on this supposition can we account for the contrasts to which attention has been directed. As to the nature of this factor, a certain amount of guidance can be obtained from a consideration of tautomerism in relation to certain other properties of the systems under review. It seems reasonable, *a priori*, to assume as a condition of first importance in the determination of mobility that the  $\alpha$ -hydrogen atom should be capable of being easily detached from the tautomeric

system. In the carboxyl and *ac*nitro-groups (systems i and ii), the mobility of which is probably much greater than in any other case, we have clear evidence of the easy detachment of the mobile hydrogen atom in the facility with which it can be replaced by an alkyl group (esterification). The mobile hydrogen atom in diazo-aminobenzene can also be replaced by an alkyl group, but it is necessary in this case to use alcoholic sodium ethoxide and an alkyl iodide, just as in the alkylation of unsymmetrical systems such as that present in ethyl acetoacetate. The same is true of amidines and glutaconic esters. It will be observed that in all these cases the systems capable of alkylation are mobile systems. On the other hand,  $\alpha$ , $\gamma$ -diphenylpropene (although formally so similar to glutaconic acid) and benzylidenebenzylamine cannot be alkylated by the ordinary methods; both these types are non-tautomeric. Evidently, the concurrence is far-reaching, but to what extent it will hold in border-line cases such as that of indene, which is alkylated with difficulty, it remains for future experiments to show. Indene, and the analogues of indene and of glutaconic acid containing the system  $\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}\cdot$  in place of  $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot$ , are cases the examination of which is in progress.

From the above parallelism it is possible to draw two conclusions relating to the conditions necessary for the activation of a potentially tautomeric system: (a) that the activating condition is dependent primarily on the  $\alpha$ -atom of the system, and is associated with the easy detachment of hydrogen from this position; (b) that the activating condition is one of the well-recognised group of related characteristics generally supposed to be associated with negative electrical polarity. Hence it is that the greatest mobility is observed when the  $\alpha$ -atom is oxygen (systems i and ii), intermediate mobility when it is nitrogen (systems iii and iv), and least mobility when it is carbon (systems v and vi); hence, also, the fact that in the last case mobility is only observed when a definite negative polarity is "induced" by strongly polar attached groups, as in the glutaconic acids. It must be admitted that questions of polarity are but little understood at present, and that much more information is required before the somewhat approximate generalisations given above can be replaced by a precise statement of the conditions for tautomerism, the complete elucidation of which forms the object of researches now in progress.

#### EXPERIMENTAL.

##### (A)—Preparation of *m*- and *p*-Nitrobenzylamine.

These bases were prepared by Gabriel's method. Hafner (*Ber.*, 1890, 23, 338) has prepared *p*-nitrobenzylamine in this way, but

gives no details. In preparing large quantities, it was found convenient to hydrolyse the phthalimides by sulphuric acid, in place of hydrochloric acid at  $200^{\circ}$ , the reagent employed by Gabriel.

The phthalimides were prepared by heating the appropriate nitrobenzyl chlorides with potassium phthalimide for half an hour by means of an oil-bath, the temperature of which was gradually raised during this period from  $100^{\circ}$  to  $115^{\circ}$ . It is essential to adhere to these conditions, as otherwise, either condensation may not take place, or the whole mass may suddenly carbonise with large evolution of gas. In any case, it is advisable to keep the mixture under close observation and add water at the first signs of self-heating. The product was isolated in the manner described by Gabriel (*Ber.*, 1887, **20**, 2227) for the ortho-compound.

The crude washed phthalimide, dissolved in the minimal quantity of cold concentrated sulphuric acid, was treated with water until the precipitate first formed just failed to redissolve. The solution was heated until a test portion gave no precipitate on cooling and diluting with water, then diluted, rendered strongly alkaline with sodium hydroxide, and extracted with ether. The base was extracted from the ether by dilute hydrochloric acid, from which it was recovered in the form of its hydrochloride by evaporation.

(B)—*Preparation of Isomeric m-Nitro-, p-Nitro-, and mp-Dinitro-derivatives of Benzylidenebenzylamine.*

*General Method of Preparation.*—Equivalent quantities of the appropriate aldehyde and amine were mixed in ethereal solution at the ordinary temperature. The ether was allowed to evaporate and the product crystallised.

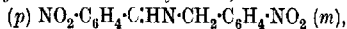
*General Properties.*—The following six substances are stable towards water and dilute alkalis, but are hydrolysed by mineral acids into the aldehyde and amine from which they were formed.

*Benzylidene-p-nitrobenzylamine*,  $C_6H_5 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol in dense prisms, m. p.  $71^{\circ}$  (Found: C = 70.0; H = 5.4.  $C_{14}H_{12}O_2N_2$  requires C = 70.0; H = 5.0 per cent.).

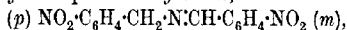
*p-Nitrobenzylidenebenzylamine*,  $C_6H_5 \cdot CH_2 \cdot N:CH \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol or ligroin in laminae, m. p.  $56^{\circ}$  (Found: C = 70.3; H = 5.4 per cent.).

*Benzylidene-m-nitrobenzylamine*,  $C_6H_5 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , separates from alcohol in short, dense prisms, m. p.  $42^{\circ}$  (Found: C = 69.8; H = 5.2 per cent.).

*m-Nitrobenzylidenebenzylamine*,  $C_6H_5 \cdot CH_2 \cdot N:CH \cdot C_6H_4 \cdot NO_2$ , separates from alcohol in long, thin laminae, m. p.  $62^{\circ}$  (Found: C = 70.1; H = 5.3 per cent.).

*p*-Nitrobenzylidene-*m*-nitrobenzylamine,

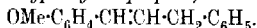
crystallises from ethyl acetate in colourless needles, m. p. 115° (Found: N = 14.7.  $\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_2$  requires N = 14.7 per cent.). This m. p. is the same as that of the next compound, but a mixture of the two melted below 100°.

*m*-Nitrobenzylidene-*p*-nitrobenzylamine,

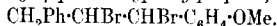
crystallises from ethyl acetate in needles, m. p. 115° (Found: N = 14.8 per cent.).

(C)—*Condensation of  $\beta$ -Phenylpropionic Acid with Anisaldehyde; Formation of p-Methoxy- $\alpha$ -benzylcinnamic Acid and  $\alpha$ -Phenyl- $\gamma$ -p-methoxyphenyl- $\Delta^2$ -propene.*

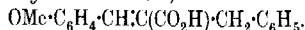
Sodium  $\beta$ -phenylpropionate (150 grams = 1 mol.), anisaldehyde (105 grams = 1 mol.), and acetic anhydride (105 grams = 1.2 mols.) were heated together for nine hours at 152°. The product was poured into an excess of sodium carbonate solution, distilled in a current of steam to remove the excess of anisaldehyde, and extracted with ether.

 *$\alpha$ -Phenyl- $\gamma$ -p-methoxyphenyl- $\Delta^2$ -propene,*

—The viscous, yellow oil which remained when the ether was dried and evaporated consisted largely of the methoxy-hydrocarbon, but it also contained a little anisaldehyde and some material which decomposed on distillation. After two distillations the methoxy-hydrocarbon was obtained as a colourless oil which boiled constantly at 227°/30 mm. (Found: C = 85.4; H = 7.3.  $\text{C}_{16}\text{H}_{16}\text{O}$  requires C = 85.7; H = 7.2 per cent.). The substance was characterised by means of its dibromo-additive product.

 *$\beta$ - $\gamma$ -Dibromo- $\alpha$ -phenyl- $\gamma$ -p-methoxyphenylpropane,*

—Two grams of the methoxy-hydrocarbon, dissolved in 2 c.c. of chloroform and cooled to 0°, decolorised 5.8 c.c. of a solution of bromine in chloroform containing 0.253 gram per c.c. (theoretical for  $2\text{Br} = 5.67$  c.c.). No perceptible amount of hydrogen bromide was evolved. The bromo-compound, which crystallised from the chloroform (a second crop was obtained after concentration), melted at 115°, and recrystallisation from light petroleum did not alter this melting point (Found: Br = 41.8.  $\text{C}_{16}\text{H}_{16}\text{OBr}_2$  requires Br = 41.6 per cent.). The compound forms stout prisms terminated by pyramids; it is easily soluble in the usual organic solvents.

*p-Methoxy- $\alpha$ -benzylcinnamic Acid,*

—The alkaline solution from which the methoxy-hydrocarbon was

extracted was heated to the boiling point, treated with excess of hydrochloric acid, and the precipitated acids collected while hot. Most of the  $\beta$ -phenylpropionic acid passed through the filter as an oil, and the remainder was removed after cooling by washing with a little cold alcohol. The residue, which consisted of a mixture of *p*-methoxycinnamic acid and *p*-methoxy- $\alpha$ -benzylcinnamic acid, was heated on the steam-bath for ten minutes with 100 c.c. of 2*N*-aqueous sodium carbonate. *p*-Methoxy- $\alpha$ -benzylcinnamic acid is only slowly soluble in dilute sodium carbonate, which, under the conditions described, dissolved all the *p*-methoxycinnamic acid but only part of the *p*-methoxy- $\alpha$ -benzylcinnamic acid; the undissolved portion was collected and recrystallised from ethyl alcohol (12 grams). The acids dissolved by the sodium carbonate were fractionally precipitated by the addition of successive portions of 10 c.c. of 2*N*-hydrochloric acid. The first two precipitations yielded *p*-methoxy- $\alpha$ -benzylcinnamic acid sufficiently free from *p*-methoxycinnamic acid to be capable of complete purification by crystallisation from alcohol (9.7 grams). The third and fourth precipitations gave mixtures which, when combined and subjected to a second series of fractional precipitations, gave 2.0 grams of *p*-methoxy- $\alpha$ -benzylcinnamic acid. The residual alkaline solutions were treated with excess of hydrochloric acid, and the recovered *p*-methoxycinnamic acid was crystallised from alcohol. In all, 23.7 grams of pure *p*-methoxy- $\alpha$ -benzylcinnamic acid were obtained along with 14.5 grams of pure *p*-methoxycinnamic acid.

*p*-Methoxy- $\alpha$ -benzylcinnamic acid crystallises from alcohol in colourless, flattened needles, m. p. 170°. It is readily soluble in aqueous sodium hydroxide, but dissolves only slowly in hot sodium carbonate solution and is evidently an unusually weak acid. It instantly decolorises cold alkaline permanganate, giving anisic acid, phenylacetic acid, and benzoic acid (Found: C = 75.9; H = 6.1.  $C_{17}H_{16}O_3$  requires C = 76.1; H = 6.1 per cent.).

The *anilide* was obtained by adding a small excess of aniline to the chloride of *p*-methoxy- $\alpha$ -benzylcinnamic acid, which was prepared by digesting the acid with thionyl chloride. It crystallised from alcohol in long, silky needles, m. p. 159° (Found: C = 80.2; H = 6.4.  $C_{23}H_{21}O_2N$  requires C = 80.4; H = 6.1 per cent.).

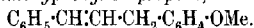
(D)—*Condensation of p-Methoxy- $\beta$ -phenylpropionic Acid with Benzaldehyde; Formation of  $\alpha$ -p-Methoxybenzylcinnamic Acid and  $\gamma$ -Phenyl- $\alpha$ -p-methoxyphenyl- $\Delta^2$ -propene.*

*p*-Methoxy- $\beta$ -phenylpropionic acid was prepared by Perkin's method from anisaldehyde (T., 1877, 31, 408, 411).

Sodium *p*-methoxy- $\beta$ -phenylpropionate (110 grams), benzaldehyde

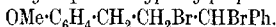
(70 grams), and acetic anhydride (70 grams) were heated together for nine and a half hours at  $150^{\circ}$ , and then poured into an excess of aqueous sodium carbonate and distilled in a current of steam to remove the excess of benzaldehyde.

*$\gamma$ -Phenyl- $\alpha$ -p-methoxyphenyl- $\Delta^2$ -propene,*



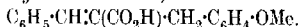
—This was isolated by extracting the alkaline liquid with ether, and purified by fractional distillation. The more volatile fractions contained benzaldehyde, but after two distillations the methoxy-hydrocarbon was obtained as a colourless, and nearly odourless oil, b. p.  $220^{\circ}/25$  mm. (Found: C = 84.7; H = 7.2.  $\text{C}_{16}\text{H}_{18}\text{O}$  requires C = 85.7; H = 7.2 per cent.). It was characterised by means of its dibromo-additive product.

*$\beta$  $\gamma$ -Dibromo- $\gamma$ -phenyl- $\alpha$ -p-methoxyphenylpropane,*



—This substance was prepared by the action of two atoms of bromine on the above methoxy-hydrocarbon in chloroform solution at  $0^{\circ}$ , the experiment being conducted just as in the case of the isomeric bromo-compound (p. 2386). The new compound separated from ligroin in colourless prisms, m. p.  $76^{\circ}$  (Found: Br = 41.8.  $\text{C}_{16}\text{H}_{16}\text{OBr}_2$  requires Br = 41.6 per cent.).

*$\alpha$ -p-Methoxybenzylcinnamic Acid,*



—The alkaline liquid from which the above methoxy-hydrocarbon had been extracted was heated to boiling and acidified with hydrochloric acid, which precipitated an oil consisting of a mixture of cinnamic acid, *p*-methoxy- $\beta$ -phenylpropionic acid, and  $\alpha$ -p-methoxybenzylcinnamic acid. The last is much less soluble in boiling water than either of the others. The oil was separated from the aqueous layer, boiled with two litres of water, and the undissolved portion, which had solidified, was collected and crystallised twice from alcohol, from which 16 grams of pure  $\alpha$ -p-methoxybenzylcinnamic acid separated in colourless, glistening needles, m. p.  $165^{\circ}$  (Found: C = 76.3; H = 6.4.  $\text{C}_{17}\text{H}_{16}\text{O}_3$  requires C = 76.1; H = 6.1 per cent.). The aqueous liquids deposited a mixture of cinnamic acid and *p*-methoxy- $\beta$ -phenylpropionic acid on cooling.

$\alpha$ -p-Methoxybenzylcinnamic acid instantly decolorises cold alkaline permanganate, forming *p*-methoxyphenylacetic acid, aniseic acid, and benzoic acid. Like its isomeride (p. 2386), it is a very weak acid: it is insoluble in cold sodium carbonate solution, although it dissolves slowly on boiling; it is easily soluble in sodium hydroxide.

The *anilide*, obtained by adding a small excess of aniline to the acid chloride, which was prepared by digesting the acid with thionyl

chloride, crystallised from alcohol in short, thick prisms or, occasionally, in needles, m. p. 140–141° (Found: C = 80.4; H = 6.6.  $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}$  requires C = 80.4; H = 6.1 per cent.).

We desire to thank the Royal Society for defraying a large part of the cost of this work.

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### CCLXXXVIII.—Dyes Derived from "Saccharin."

#### *The Sulphamphthaleins.*

By SIKHIBHUSHAN DUTT.

A NUMBER of sulphonephthaleins have already been prepared by the aid of *o*-sulphobenzoic acid (Remsen, *J. Amer. Chem. Soc.*, 1885, **7**, 180; compare also *ibid.*, 1887, **9**, 372; Blackshear, *ibid.*, 1892, **14**, 455; Remsen and MacKee, *ibid.*, 1896, **18**, 794; Lubs and Clark, *J. Washington Acad. Sci.*, 1915, **5**, 609).

The difficulty of getting pure *o*-sulphobenzoic acid in good yield led the author to investigate the action of "saccharin" on amines and phenols. In this way, condensation products have been obtained which are characterised by their colour and fluorescence and closely resemble the corresponding phthaleins in constitution and behaviour. They differ from the corresponding sulphonephthaleins in having the bivalent imido-group in place of the lactone oxygen atom. Accordingly, they have been named *sulphamphthaleins*.

The trimethyl derivative of phenolsulphamphthalein is obtained by the action of methyl sulphate on the trisodium salt, but only the diacetyl and the dibenzoyl derivatives are obtained by similar treatment with acetyl chloride and benzoyl chloride, respectively. The diacetyl derivative is more conveniently obtained by the action of acetic anhydride and pyridine on phenolsulphamphthalein itself.

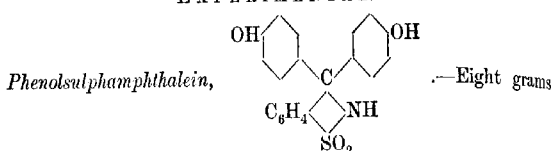
The following amino- and hydroxy-compounds have been condensed with "saccharin": phenol, resorcinol, orcinol, phloroglucinol, hydroxyquinol, catechol, 1:2:4:5-tetrahydroxybenzene, *m*-phenylenediamine, *m*-aminophenol, *m*-dimethylaminophenol, and 4:6-diaminoresorcinol. The colour and dyeing properties of the products closely resemble those of the corresponding phthaleins, but the fluorescence is somewhat stronger. They all decompose on heating.

The "saccharin" employed in the above-mentioned condensations was obtained by extracting the commercial material with sodium hydrogen carbonate, treating the solution with hydro-



chloric acid, and fractionally crystallising the precipitate from ether, the portion melting at 218–220° being utilised.

## EXPERIMENTAL.



of "saccharin," 15 grams of phenol, and 5 c.c. of concentrated sulphuric acid were heated together at 100–110° for ten hours. The excess of phenol was distilled off in steam, and the brownish-red residue purified by dissolving it in ammonia and treating the filtered solution with dilute hydrochloric acid. The precipitate crystallised from hot water in yellow prisms, which became red on rubbing. The yield was 15 per cent. of the theoretical. With zinc chloride at 160° as the condensing agent, the yield is only 6 per cent.

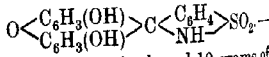
Like phenolphthalein, phenolsulphamphthalein dissolves in alkali with a pink colour. It dissolves in water, acetic acid, or alcohol with a yellow colour, but is insoluble in ether. It has been obtained in two chromoisomeric forms, yellow and red, the former being the more unstable (Found : S = 9.1; N = 4.1.  $C_{19}H_{15}O_4NS$  requires S = 9.1; N = 3.9 per cent.).

The *trisodium* salt, prepared by neutralising an aqueous solution of the sulphamphthalein with N/2-sodium hydroxide (3 equivalents were required) and evaporating the solution to dryness, is a dark red, crystalline substance, which dissolves in water with a brilliant pink colour and is extremely hygroscopic.

The *trimethyl* derivative was prepared by the action of methyl sulphate on the trisodium salt. It crystallises from dilute acetic acid in colourless needles melting at 142° (Found : C = 67.5; H = 5.6.  $C_{22}H_{21}O_4NS$  requires C = 67.8; H = 5.3 per cent.).

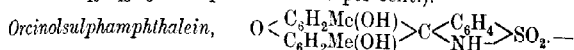
A *dibenzoyl* derivative was prepared by the action of benzoyl chloride on the sodium salt. It crystallises from hot water in colourless, silky needles melting at 127° (Found : C = 70.5; H = 4.2.  $C_{33}H_{24}O_6NS$  requires C = 70.7; H = 4.3 per cent.).

The *diacetyl* derivative, prepared by means of acetic anhydride and pyridine, crystallises from dilute alcohol in colourless needles, m. p. 112° (Found : C = 62.8; H = 4.4.  $C_{23}H_{19}O_6NS$  requires C = 63.15; H = 4.3 per cent.).

*Resorcinolsulphamphthalein*,  .—Eight grams of "saccharin," 11 grams of resorcinol, and 10 grams of

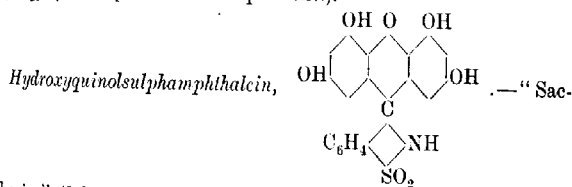
fused zinc chloride were heated at 180—190° for two hours, when the melt became almost solid. The cooled product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, washed with water, and extracted with ether to remove unchanged "saccharin." The product was converted, by the action of lead acetate on the sodium salt, into the lead lake, which was dried, suspended in absolute alcohol, and decomposed by hydrogen sulphide. The alcoholic solution was filtered, concentrated to a small volume, and the dye precipitated with ether, being obtained in microscopic, brownish-yellow needles.

*Resorcinolsulphamphthalein* is very soluble in alcohol or acetic acid, moderately soluble in water, and insoluble in ether or light petroleum. It dissolves in alkali with an orange colour, and the solution on dilution shows a very intense yellowish-green fluorescence. The sodium salt dyes light yellow shades on wool (Found: S = 8.4.  $C_{19}H_{13}O_5NS$  requires S = 8.7 per cent.).



Eight grams of "saccharin," 13 grams of orcinol, and 11 grams of fused zinc chloride were heated at 180° for about three hours, and the product was isolated as described above. It crystallises from dilute alcohol in brownish-yellow needles and dissolves in alkali with a blood-red colour, the solution, on dilution, showing a brilliant green fluorescence. The sodium salt dyes pink shades on wool (Found: S = 7.9.  $C_{21}H_{17}O_5NS$  requires S = 8.1 per cent.).

*Phloroglucinolsulphamphthalein*.—Prepared from 3.6 grams of "saccharin," 5 grams of phloroglucinol, and 4 grams of fused zinc chloride at 180—190° in about twenty minutes, and isolated in the manner already described, this compound crystallised from hot water in long, brownish-yellow needles. It dissolves in alkali with an orange-red colour, but the solution is not fluorescent. The sodium salt dyes fine orange shades on wool (Found: S = 8.3.  $C_{19}H_{13}O_7NS$  requires S = 8.0 per cent.).



charin" (1.8 grams), hydroxyquinol (2.5 grams), and fused zinc chloride (2 grams) were heated at 160—170° for two hours while a slow stream of dry hydrogen was passed over the molten mass. Purification by means of sodium hydroxide solution having been

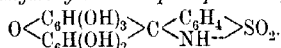
found ineffective, the product was acetylated. The *acetyl* derivative crystallised from dilute alcohol in colourless prisms melting above 300°. The product of its hydrolysis by alkali crystallises from a mixture of alcohol and ether in light reddish-brown, silky needles.

*Hydroxyquinolsulphamphthalein* is very soluble in alcohol or acetic acid, moderately soluble in hot water, and sparingly soluble in ether or cold water. It dissolves in alkali with a pink colour, the solution showing a feeble yellow fluorescence. The sodium salt dyes fine pink shades on wool (Found: S = 7.8.  $C_{19}H_{13}O_7NS$  requires S = 8.0 per cent.).

*Catecholsulphamphthalein*.—Eight grams of "saccharin," 11 grams of catechol, and 10 grams of fused zinc chloride were heated at 180–190° for three hours. The cold product was powdered, washed with concentrated hydrochloric acid, and crystallised from ether, minute brown needles being obtained.

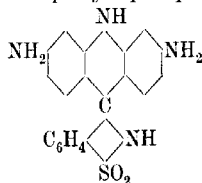
*Catecholsulphamphthalein* is very soluble in water, alcohol, or acetic acid, and sparingly soluble in ether. It dissolves in alkalis with a green colour (Found: S = 8.6.  $C_{19}H_{13}O_5NS$  requires S = 8.7 per cent.).

1 : 2 : 4 : 5-Tetrahydroxybenzenesulphamphthalein,



—"Saccharin" (0.8 gram) and 1 : 2 : 4 : 5-tetrahydroxybenzene (1.4 grams) were heated at 160° with 0.5 gram of fused zinc chloride for about two hours. The product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, dried, and acetylated by the usual method. The *hexa-acetyl* derivative crystallised from dilute acetic acid in white, silky needles which did not melt at 290° (Found: C = 54.1; H = 3.6.  $C_{31}H_{25}O_{15}NS$  requires C = 54.5; H = 3.7 per cent.). On hydrolysis with alkali, the pure dyestuff was obtained, which crystallised from hot water in dark brown needles with a green, metallic lustre. It dissolves in alkali with a pink colour but without fluorescence (Found: S = 7.0.  $C_{19}H_{13}O_5NS$  requires S = 7.4 per cent.).

4 : 4'-Diamino-2 : 2'-iminophenylsulphamphthalein,

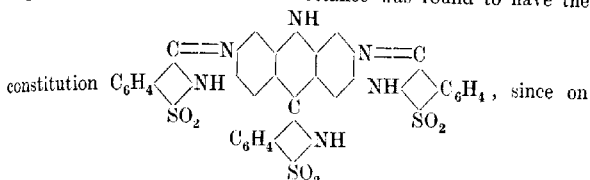


—"Saccharin" (1.8 grams) and *m*-phenylenediamine hydrochloride

(3.6 grams) were heated at  $230^{\circ}$  for about fifteen minutes. The melt was extracted with ether to remove unchanged "saccharin" and dissolved in hot alcohol. The alcoholic solution, on cooling, deposited a quantity of brown needles, which were removed. The mother-liquor was concentrated to small bulk and cautiously diluted with water, when the sulphamphthalein was deposited in bright yellow, prismatic needles (Found: S = 8.7; N = 15.1.  $C_{16}H_{16}O_2N_4S$  requires S = 8.7; N = 15.4 per cent.).

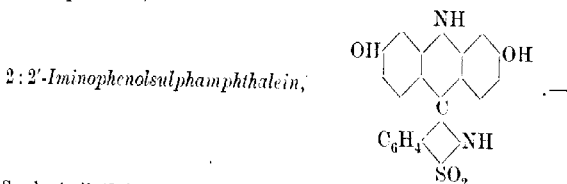
The substance is very soluble in alcohol or acetic acid, sparingly soluble in water, and insoluble in ether. Its solution shows an intense yellow-green fluorescence, which is very similar to that of fluorescein.

The above-mentioned brown substance was found to have the



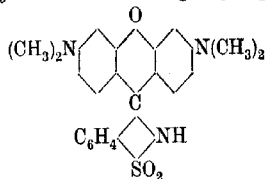
boiling with alkali it decomposed yielding "saccharin" and the diaminoiminophenylsulphamphthalein. It was also formed when these two substances were heated with zinc chloride at  $160^{\circ}$ .

It is slightly soluble in alcohol or acetic acid, and insoluble in water or ether. The solution shows a brilliant green fluorescence (Found: S = 13.4; N = 12.3.  $C_{33}H_{22}O_6N_6S_3$  requires S = 13.8; N = 12.1 per cent.).



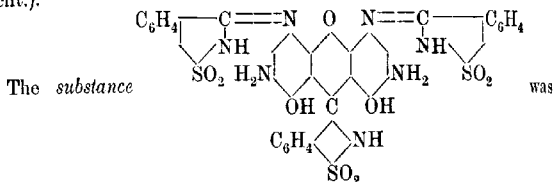
"Saccharin" (3.6 grams), *m*-aminophenol (4.5 grams), and fused zinc chloride (4 grams) were heated at  $180-190^{\circ}$  for two hours. The melt was dissolved in dilute caustic soda and the filtered solution precipitated with hydrochloric acid. The compound, which could not be crystallised, was purified by means of the lead lake, as described in the case of the resorcinol compound. It is a dark brown substance which dissolves in alkali with a brown colour, but without fluorescence. Its solutions in alcohol and acetic acid show a fine moss-green fluorescence (Found: N = 7.2.  $C_{19}H_{14}O_4N_2S$  requires N = 7.6 per cent.).

## 4 : 4'-Tetramethyldiamino-2 : 2'-oxidophenylsulphamphthalein,



—“Saccharin” (1·8 grams), *m*-dimethylaminophenol (2·8 grams), and fused zinc chloride (1·5 grams) were heated at 180—190° for about one hour, when the melt assumed a deep pink colour and solidified completely. The product was powdered and boiled with alcohol and a little bone black; the filtered solution slowly deposited the condensation product in small, pink needles with a golden lustre.

The substance is very soluble in alcohol, acetic acid, or ether, slightly in water, and dissolves in dilute mineral acids with a pink colour and a strong yellow fluorescence. It dyes fine pink shades on wool (Found: S = 7·5.  $C_{23}H_{23}O_3N_3S$  requires S = 7·6 per cent.).



prepared by heating 1·8 grams of “saccharin,” 4·5 grams of 4 : 6-diaminoresorcinol hydrochloride, and 3 grams of fused zinc chloride at 160° for three hours while a slow stream of dry hydrogen was passed over the molten mass. The cold product was finely powdered, digested with concentrated hydrochloric acid for half an hour, and purified by means of the lead lake. It could not be crystallised. It is a dark brown substance which dissolves in alkali with a splendid blue colour, but without fluorescence (Found: S = 12·8.  $C_{33}H_{23}O_9N_7S_3$  requires S = 12·7 per cent.).

Further work in this direction is in progress.

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CCLXXXIX.—*The Viscosity of Cellulose. Part II. The Lowering of the Viscosity of Cellulose by Various Reagents.*

By REGINALD ARTHUR JOYNER.

It was during the war that the importance became recognised of having cellulose of a definite viscosity, the value of which depended on the use to which the nitrated or acetylated cellulose was to be put. In this vol., p. 1511, was described a modification of the method adopted by Gibson, Spencer, and McCall for the determination of the viscosity in cuprammonium hydroxide, and the effect on the viscosity of varying the concentration of the copper, ammonia, and cellulose was given. The present paper deals with the lowering of the viscosity of cellulose itself by various reagents.

The first definite work published on the effect of solutions of sodium hydroxide on cellulose is given by Gibson (T., 1920, 117, 479). It was shown that the effect of sodium hydroxide depended on the concentration and the temperature at which the experiment was carried out.

One of the chief difficulties in work on viscosity lies in the interpretation of the results, for example, on p. 2407 is given the effect of increasing amounts of air on the viscosity of cellulose when dissolved in cuprammonium hydroxide. In the second series of experiments, with 2 per cent. solutions of cellulose, it is seen that 2.7, 13.6, and 30 c.c. of air lowered the viscosity by 530, 1300, and 1800 seconds, respectively. Although the lowering of viscosity is relatively great for the first additions of air, it is not correct to assume that the chemical effect is relatively great for the first additions. It was shown in Part I of this paper that the log. viscosity is almost directly proportional to the concentration expressed in grams per 100 c.c. of solvent, and therefore it is clear that if the agent referred to above ultimately reduces the viscosity of the cellulose to a very low figure, then the amount of cellulose transformed will be approximately given by the drop in the log. viscosity. It was shown that celluloses had constants given by a modified Arrhenius formula which were independent of the concentration. Now, the highest viscosity possible for a 2 per cent. solution of cellulose appears to be about 57,000 seconds, or 28,000 absolute units (p. 2399), whilst by repeatedly kieriing a cellulose with sodium hydroxide a viscosity of 1 second for a 5 per cent. solution was obtained. These two figures give constants of 2.78

and 0.15, respectively, which denote the limits for the viscosity of cellulose for a 2 per cent. solution. The hypothesis is now made that there are two kinds of cellulose, high-viscosity cellulose or cellulose "A," which has the higher of the above constants, and low-viscosity cellulose or cellulose "B," which has the lower of the above constants. A cotton which has an intermediate viscosity is a mixture of these two kinds, and the high-viscosity cellulose content will be given by the equation  $x = (\eta - 0.15)/2.63$ , where, by the Arrhenius formula,  $\theta = \log \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}$  / concentration. In this formula, instead of the log. viscosity of solvent, a number, -0.30, is used, so that

$$\theta = \frac{\log \text{viscosity of solution} + 0.80}{\text{concentration (gram per 100 c.c. of solvent)}}$$

#### EXPERIMENTAL.

In order to have a standard substance to work with, a large batch of sliver cotton was obtained which gave the following results when tested by routine methods: moisture, 4.62; oily matter, 0.24; mineral matter, 0.71; solubility in 3 per cent. NaOH at 100°, 5.66; copper reduction number,\* 0.11 per cent; dyeing test, nil.

Raw sliver is only partly soluble in cuprammonium hydroxide, but becomes quite soluble after being acted upon by dilute sodium hydroxide, which destroys the protein matter present.

In carrying out the experiments on the action of sodium hydroxide on cellulose, the following procedure was adopted. The cotton was placed in test-tubes, a quantity of the solution of sodium hydroxide or of other substances added, and the cotton worked in the liquid or evacuated to expel the occluded air; the tubes were then filled to a convenient height and sealed. If this procedure be not adopted, the oxygen in the presence of caustic soda will oxidise the cellulose and lower its viscosity. The tubes were then heated in an autoclave at a definite temperature for a definite time. It was found that the temperature of the autoclave could be kept constant to within 1° or 2° for long periods. The autoclave was then opened, the liquor in the tubes titrated, and the cotton washed with dilute acetic acid and thoroughly with water, and finally dried at about 70°. The ratio of liquor to cellulose in the tubes was varied from 15 to 10. The lower ratio could be

\* The copper reduction number is the weight in grams of cuprous oxide reduced by 100 grams of cotton from a solution of the following composition in grams per litre: hydrated copper sulphate 17.3, anhydrous sodium carbonate 100, anhydrous sodium citrate 130. This and the soda-soluble figure give the amount of degraded cellulose present.

decreased considerably without making any difference in the results. Duplicate experiments were often carried out. All the determinations of the viscosity were made at  $20^{\circ} \pm 1^{\circ}$  for a 2 per cent. solution of cellulose, unless otherwise stated.

Table I gives the results obtained when the time of heating was nine hours.

TABLE I.

Showing the effect of varying concentration of sodium hydroxide on sliver cotton when heated for nine hours at the temperatures stated.

100°.			110°		
Normality of NaOH.	Viscosity (sec.).	Cellulose "A."	Normality of NaOH.	Viscosity (sec.).	Cellulose "A."
1.0	5760	81	0.91	2090	73
4.5	1725	71	1.85	1161	68
6.7	425	59	1.84	1203	68
6.7	394	59	2.81	423	60
			3.20	126	49
	125°		3.28	133	49
0.44	950	66	5.49	56	43
0.53	930	66	5.43	53	43
0.96	740	64	6.94	15.6	32
0.96	780	64	6.92	15.4	32
2.92	56	43			
2.92	53	43		134°	
5.52	38	23	0.25	675	62
			0.5	354	58
	141°		1.0	175	52
0.0	350	58	2.0	59	43
0.0	332	58	3.0	9	28
0.17	255	55	4.5	1.4	12
0.17	369	58			
0.44	96	47			
0.43	95	47			
0.90	28	37			
0.86	29	37			

The results shown in Table I have been plotted in Fig. 1, and a series of nearly straight lines is the result. The higher the temperature the more these slope to the left, showing an increasing rate of reaction. These lines, on extrapolation for a zero concentration of sodium hydroxide, cut the abscissa at increasing distances to the left. This denotes that water alone must have some effect on the cotton and that this effect increases rapidly with the temperature.

In order to study the effects of the lower concentrations of caustic soda in more detail, sliver was heated for six and a half hours at  $130^{\circ}$  and a kiered sliver having a viscosity of 314 seconds was heated at the same temperature for five hours. The results are given in Table II.



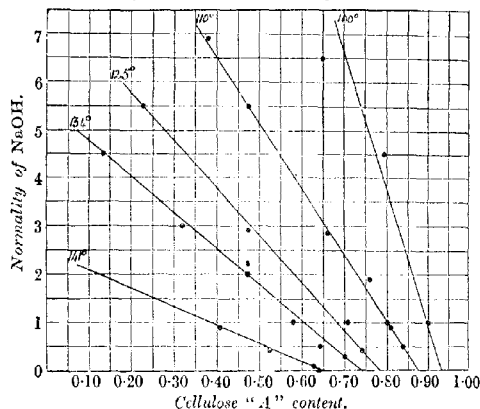
TABLE II.

Showing the effect of low concentrations of caustic soda on sliver when heated at 130° for six and a half hours, and on a kiered sliver, viscosity 314 seconds at 130°, when heated for five hours.

Sliver.			Kiered sliver.		
Normality of NaOH.	Viscosity (sec.).	Cellulose "A" per cent.	Normality of NaOH.	Viscosity (sec.).	Cellulose "A" per cent.
2.17	67, 55	44, 43	2.0	29, 27	37, 37
0.96	105, 126	48, 49	1.0	52, 48	41, 41
0.49	155	51	0.50	57, 50	41, 41
0.24	255	55	0.25	93, 92	42, 42
0.091	356, 358	58, 58	0.10	116, 118	42, 42
0.044	410	59			
Water	413, 476	59, 60	Water	170, 161	43, 43

FIG 1.

Showing the effect of heating sliver with various solutions of sodium hydroxide for nine hours at the temperatures stated.



The results in Table II are shown graphically in Fig. 2, and it is evident the more dilute concentrations of caustic soda have a relatively greater effect than the more concentrated ones. This makes it seem probable that the effect is due to the hydroxyl ions.

The results which have been obtained on the action of sodium hydroxide on cellulose are important from the practical point of view in the kierung of cotton. The concentrations of sodium hydroxide used are generally not more than 4 per cent., and therefore the drop in viscosity can be found for any temperature between 100° and 140° for a kierung period of nine hours. The results for

the various concentrations of sodium hydroxide have been plotted against the temperature in Fig. 3, and it will be seen that when the temperature is lowered the curves become more vertical and approach each other. The extrapolated value of the log. viscosity for the point where they become vertical and touch each other is about 4.75. This means that the maximum value for the viscosity of cellulose is about 57,000 seconds, or 28,000 C.G.S. units at 20° for a 2 per cent. solution in cuprammonium hydroxide containing 13 grams of copper and 200 grams of ammonia per litre.

#### Kinetic Measurements in Presence of Sodium Hydroxide.

Kinetic measurements were carried out, using *N*-sodium hydroxide at various temperatures. In order to eliminate errors due to fluctuating temperature, which would be very difficult to prevent when using an autoclave which could only be heated and cooled slowly, three samples of cellulose having different viscosities were heated for seven hours, simultaneously, at various temperatures. After cooling and washing, the viscosities of the samples were re-determined, and the amount of change, as denoted by the amount of cellulose "A" transformed, was calculated. It is seen that the amount of change in each case is proportional to the amount of cellulose "A" originally present; in other words, the reaction proceeds as though it were unimolecular. The results are given in Table III, *k* hours being calculated for a unimolecular reaction,  $k = 1/t. \log a/a - x$ .

FIG. 2.

Showing effect of heating (1) raw sliver for six and a half hours at 130°, (2) cleaned sliver for five hours at 135°, with different concentration of sodium hydroxide.

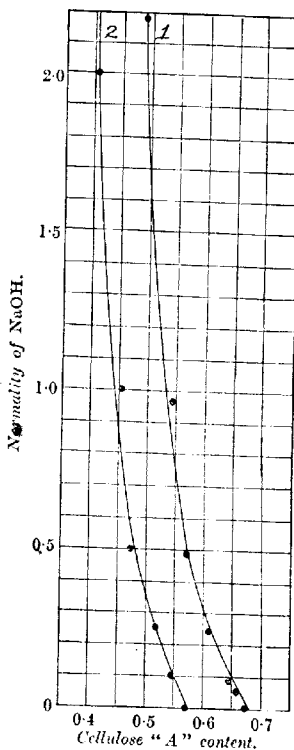
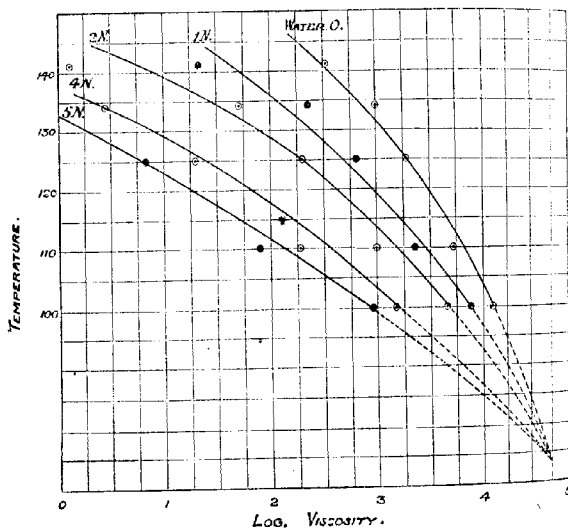


TABLE III.

Showing the calculation of the unimolecular constant,  $k$ , for the action of  $N$ -NaOH on cellulose at various temperatures. Time of heating, seven hours.

Initial viscosity.	Initial cellulose "A" per cent.	Final viscosity.	Final cellulose "A" per cent.	$k$ (hours).	Temp.
1440	69.5	342	57.5	0.0270	116°
240	54.8	84.5	46.1	0.0247	
69	44.5	28.3	37.0	0.0264	
1440	69.5	248	54.8	0.0339	125°
240	54.8	58.2	42.9	0.0349	
69	44.5	23.9	35.6	0.0319	
1440	69.5	67.8	44.2	0.0647	137°
240	54.8	26.2	36.3	0.0589	
69	44.5	10.1	28.5	0.0603	
1440	69.5	10.2	28.6	0.127	146°
240	54.8	6.5	24.8	0.113	
69	44.5	4.6	22.1	0.100	

FIG. 3.



With the exception of the result at the higher temperatures, the constant obtained is fairly satisfactory.

The result found here agrees with many heterogeneous reactions in giving a unimolecular constant, a list of which is given in "A

System of Physical Chemistry," Part I, p. 450, William C. McC. Lewis. As regards the nature of the reaction, the results obtained by Armstrong (*Proc. Roy. Soc.*, 1904, **73**, 508) on the action of enzymes on sugar are of interest. The temperature coefficient for the results with cellulose is low, a rise of  $10^{\circ}$  increasing the rate about 1.6 times, which is in accordance with many results obtained for heterogeneous reactions. This reaction is, however, different from other heterogeneous reactions in that the substance undergoing change is solid, whilst the catalyst is a liquid. From these results it is now possible to state the conditions necessary in order to lower the viscosity of cellulose of any viscosity by a required amount.

In the last experiment, along with the three samples of cleaned sliver a sample of raw sliver was also subjected to the action of N-sodium hydroxide, and thereafter the viscosity was determined. Knowing, therefore, the final amount of cellulose "A," and using the constants obtained, it was possible to calculate the amount of cellulose "A" in the pure unattacked sliver. The average values for the constant being employed in each case, except in the last, where the highest one was used, the values found were 86, 86, 82, and 83 per cent. The actual values should have been 100 per cent. in each case.

*The Selective Sorption of Sodium Hydroxide by Cellulose and its Action in lowering the Viscosity.*

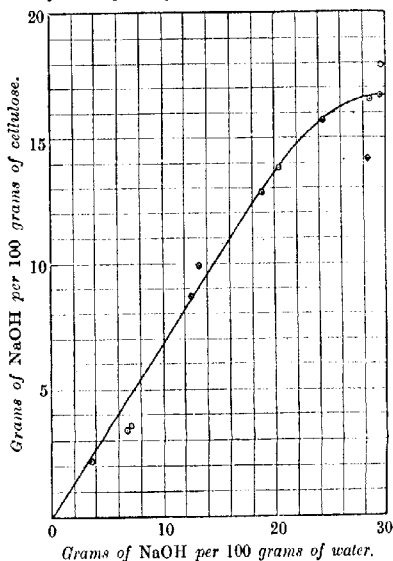
With solutions stronger than normal, the action of sodium hydroxide in lowering the viscosity has been shown to be nearly proportional to the gross concentration of the sodium hydroxide. Although this was probably accidental, depending on various factors, for example, degree of ionisation, hydration, etc., it was thought interesting to study the action from the sorption point of view, as it was known that the sorption of sodium hydroxide from aqueous solution by cellulose also increases with the concentration.

The question of the sorption of sodium hydroxide by cotton has been revised by Leighton (*J. Physical Chem.*, 1916, **20**, 32) especially from the point of view of the phase rule, and it was shown that the occurrence of definite combination between cellulose and sodium hydroxide has by no means been proved. Leighton showed that measurements involving decrease in concentration of a sodium hydroxide solution due to the addition of cotton give simply the amount of selective sorption, that is, the difference in the absorption of sodium hydroxide and water. He endeavoured to measure the total sorption by centrifuging cotton which had been placed in

sodium hydroxide solution; on the assumption that the cotton had then no solution clinging to it, the increase in weight of the cotton and the amount of sodium hydroxide therein gave the quantity of water and of sodium hydroxide sorbed. This method obviously furnished too high results, because from his experiments he deduced that 1 gram of cotton can sorb 4 grams of water, whilst in reality wet cotton can be squeezed so that the water content falls as low as 0.8 gram per gram of cotton.

FIG. 4.

Showing the sorption of sodium hydroxide by cellulose.



Vieweg (*Ber.*, 1907, 40, 3876) determined the selective sorption of sodium hydroxide from an aqueous solution by titrating a definite volume of solution before and after the addition of cotton. In the present work, in order to obtain more accurate results the analyses were done on definite weights of the solutions. Known weights of sodium hydroxide (volume 10 c.c.) and cellulose (about 1 gram) were well mixed together at room temperature and a definite weight of the solution was titrated. Preliminary experiments showed that after one and a half hours the selective sorption of the sodium hydroxide did not increase in six days. The results obtained are shown in Table IV and graphically in Fig. 4.

TABLE IV.

Giving results obtained for the selective sorption of sodium hydroxide by cotton.

Composition of aqueous phase. Grams of NaOH per 100 grams of water.	Composition of cellulose phase. Grams of NaOH per 100 grams of cellulose.
29.6	16.6, 17.8
28.6	14.1, 16.5
24.3	15.7
20.5	13.9
19.1	12.8
18.8	12.6, 12.8
13.3	9.9
12.8	8.6
7.65	3.41
6.95	3.23
4.02	1.72
3.79	2.20, 2.27, 2.15, 2.12, 2.01

These results show that sorption of sodium hydroxide by the cellulose takes place. This sorption, as will be seen, is increased by the addition of neutral salts.

Preliminary experiments on the effect of the addition of sodium chloride to the sodium hydroxide solution showed that the concentration in the cellulose phase increased, and accordingly solutions were made by adding increasing amounts of sodium chloride to sodium hydroxide. In these solutions the ratio of water to sodium hydroxide was therefore constant. The sorption from these solutions was determined and also the effect on sliver after heating for six and a half hours at 122°.

TABLE V.

Showing the effect of adding increasing amounts of salt on the sorption of sodium hydroxide by cellulose, and the relative effects of such solutions on cellulose.

Composition of solution.				Grams of NaOH per 100 grams of cellulose.		Viscosity (sec.).	Cellulose "A."
NaOH.	NaCl.	NaNO <sub>3</sub> .	water.	Grams of NaOH per litre.	Grams of NaOH per 100 grams of cellulose.		
7.1	—	—	92.9	76.5	3.41	433, 414	59
6.5	6.8	—	86.7	73.5	5.11	482	60
6.0	13.6	—	80.4	70.2	5.40	417	59
5.3	22.4	—	72.3	65.0	5.95	388	59
4.2	13.7	23.1	59.0	56.0	6.40	111, 108	48

The effect of other neutral salts was studied and it was found that neutral salts alone had little effect on raw sliver at 120°, but in conjunction with sodium hydroxide potassium chloride had a

specially strong effect. When, however, a sliver which had already been acted upon by sodium hydroxide was so treated, potassium chloride had an effect almost equal to that of an equivalent concentration of sodium or potassium hydroxide, whilst the effect of sodium chloride, sodium nitrate, barium chloride, or potassium nitrate was almost negligible at 120°. As was stated on p. 2396, raw sliver is not very soluble in cuprammonium hydroxide, and it would seem that in its natural state it contains very little free cellulose and that the protein matter must first of all be destroyed before the cellulose can be attacked.

Further results on the effects of sodium and potassium chlorides are given in Table VI.

TABLE VI.

Showing the effect of equivalent concentrations of potassium chloride and sodium chloride on sliver in seven and a half hours at 120°.

Composition of solution.	Viscosity.	Cellulose "A" per cent.
(a) 2N-NaOH	340, 326	57
(b) 2N-KOH	510, 491	61
100 c.c. of (a) with 20 grams of KCl	72, 71	45
" " " 15.9 " NaCl	445, 431	59
" (b) " 20 " KCl	82, 82	46
" " " 15.9 " NaCl	65.2	63

These results confirm the others as regards the relative effects of sodium chloride and potassium chloride. The effect of the potassium chloride may be due to its slightly increasing the hydroxyl-ion concentration, also to its raising the potential of the hydroxyl ions; it may also have a specific action on the cellulose.

It was found that the sorption of sodium chloride or potassium chloride by cellulose from 22 per cent. solutions was small, being only about 1 gram per 100 grams of cellulose.

When sliver was heated with a solution of ammonium chloride or calcium chloride, a degraded product of very low viscosity resulted, but when a mixture of ammonium chloride and ammonia was used, there was scarcely any effect. Evidently the action of the ammonium chloride or calcium chloride was due to the acid set free by hydrolysis. Ammonia solution alone also had little action.

#### *The Action of Dilute Acids on Cellulose.*

It was recognised that the action of dilute acids on cellulose was much more rapid than that of alkalis, but on account of their degrading action it was necessary to use such a strength that little or no hydrocellulose could be formed.

The following tables show the action of various strengths of hydrochloric acid in degrading cellulose at 100°.

TABLE VII.

Showing the action of various strengths of hydrochloric acid on cellulose at 100°.

Strength of acid.	Time of action.	Remarks.
N/1HCl	5 minutes	Converted to powder.
"	55 "	50% of the product soluble in 3% NaOH; viscosity of 5% sol. = 1 sec.
N/10HCl	10 "	Soluble in NaOH, 4 per cent.
"	30 "	" " 12 "
N/30HCl	30 "	" " 4 "
"	3 hours	" " 12 "
N/100HCl	3 "	" " 3 "

The experiments with acids were therefore limited to concentrations of N/30 and N/100.

In determining the rate of reaction, cellulose was boiled under reflux, at a definite time cold water was poured down the condenser to stop the reaction, and the product was well washed and dried at 70°. The viscosity, usually for a 2 per cent. solution, was determined; the percentage of cellulose "A" and the constants  $k$  for the various orders of reaction were calculated:  $k_{\text{uni}} = \frac{1}{t} \log \frac{a}{a-x}$ ;  $k_{\text{bi}} = \frac{1}{t} \left( \frac{1}{a-x} - \frac{1}{a} \right)$ ;  $k_{\text{ter}} = \frac{1}{2t} \left( \frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$ , where  $a$  = fraction of cellulose "A" at time 0 and  $a-x$  = fraction at time  $t$  minutes.

TABLE VIII.

Showing the effect of dilute hydrochloric acid on cleaned cellulose.

Time in min.	Viscosity in sec.	Fraction of cellulose "A."	$k_{\text{uni}}$	$k_{\text{bi}}$	$k_{\text{ter}}$	Remarks.
—	1480	0.697	—	—	—	
5	115	0.481	0.054	0.13	0.22	Acid N/100HCl.
10	59	0.431	0.048	0.089	0.16	T = 100°.
20	18.0	0.333	0.038	0.078	0.18	Cellulose sliver.
30	11.8	0.298	0.028	0.064	0.15	Solubility in NaOH at
55	3.5	0.198	0.023	0.065	0.22	end, 3%.
175	1.2	0.110	0.011	0.044	0.23	
—	1480	0.697	—	—	—	
5	132	0.498	0.065	0.11	0.20	Acid 0.0113N-HCl.
10	57	0.427	0.048	0.090	0.17	T = 100°.
20	17.7	0.332	0.036	0.079	0.18	Cellulose sliver.
30	8.9	0.276	0.030	0.071	0.18	
45	5.0	0.228	0.024	0.066	0.18	
60	3.7	0.204	0.020	0.057	0.18	Solubility in NaOH at
						end, 1%.



TABLE VIII (continued).

Time in min.	Viscos- ity in sec.	Frac- tion of		Remarks.	Time in min.	Viscos- ity in sec.	Frac- tion of		Remarks.
		"A."	$k_{ter}$				"A."	$k_{ter}$	
0	1480	0.697	—	Acid 0.286N.	0	1480	0.697	—	Acid
5	83.5	0.358	0.56	HCl. T=	15	727	0.638	0.0130	0.0100N.
10	22.0	0.269	0.58	100°. 2.5%	45	395	0.589	0.0092	HCl. T=
20	12.5	0.232	0.41	for viscosity	105	198	0.531	0.0070	80°.
30	6.6	0.190	0.43	except at 165	105	195	0.478	0.0070	
60	2.1	0.117	0.59	zero time.	285	47	0.411	0.0067	Sliver.
120	0.9	0.058	1.20	Sliver.	405	32.6	0.382	0.0059	
					405	29.3	0.374	0.0054	
0	224	0.491	—	Acid	0	840	0.650	—	Acid
5	72	0.405	0.19	0.0100N-HCl.	1	485	0.606	0.18	0.0100N.
10	4.5	0.368	0.16	T=100°.	4	197	0.530	0.15	HCl.
20	18.2	0.300	0.17	Linters	19	36.0	0.391	0.11	T=100°.
30	12.5	0.270	0.16	2.5% for vis-					
60	5.1	0.196	0.18	cosity.	59	5.4	0.232	0.14	Cops.
150	2.7	0.152	0.13						

It is seen that  $k_{ter}$  is fairly constant. As the concentration of the acid remains constant throughout the reaction, the number denoting the order should be increased by one, and if the reaction took place in a homogeneous phase giving a termolecular constant, the reaction would be strictly quadrimolecular. However, in view of the fact that the reaction is apparently heterogeneous it is difficult to imagine that the obtaining of the constant has the same significance as it would have if the reaction took place in a homogeneous liquid phase. The temperature effect is large and it appears that the constant is probably proportional to the acid concentration. One experiment was made with acetic acid, when an  $N/10$ -solution in fifty minutes reduced the viscosity of a cellulose from 1480 seconds to 68 seconds.  $N/100$ -Hydrochloric acid would take about ten minutes to produce the same lowering. An  $N/10$ -solution of acetic acid has about twice the effect expected from a comparison of the concentration of the hydrogen ions in  $N/100$ -hydrochloric acid.

#### *Reduction of the Viscosity of Cellulose by Oxidising Agents.*

The first experiments under this heading were made with cellulose in cuprammonium solution. The viscosity was first determined in an atmosphere of hydrogen. After one-quarter of the cellulose solution had run out, to the remainder a measured volume of air was added and the mixture well shaken for an hour, the reaction being half complete in five minutes. Blank experiments were carried on the hydrogen from time to time. The results obtained are shown in Table IX.

TABLE IX.

The quantitative effect of air on the lowering of the viscosity of cellulose cuprammonium solutions.

Seventy-five c.c. of solution were used in each experiment.

2 Per cent. solution of cellulose.						
1	2	3	4	5	6	
Viscosity before.	Cellu- lose "A" before.	Viscosity after.	Cellu- lose "A" after.	C.c. air added.	Diff. in cellu- lose "A" per c.c. of air.	Column 6. Column 2.
242	0.547	17.1	0.329	20.7	0.0105	
240	"	7.2	0.258	25.1	0.0114	
245	0.548	4.8	0.226	30.7	0.0105	
				Mean	0.0108	0.020
1420	0.694	890	0.656	2.7	0.0140	
1400	"	73	0.449	13.6	0.0180	
1790	0.773	27	0.367	21.2	0.0164	
1840	0.715	5.0	0.238	30.2	0.0158	
				Mean	0.0161	0.023
67.4	0.443	43.0	0.405	3.9	0.0097	
66.4	"	27.0	0.368	8.5	0.0087	
70.0	0.447	10.1	0.286	16.4	0.0098	
72.8	0.450	4.7	0.223	25.6	0.0101	
				Mean	0.0096	0.021
4 Per cent. solution of cellulose.						
2650	0.375	1850	0.348	6.3	0.0043	
1680	0.333	512	0.283	15.9	0.0030	
2730	0.354	220	0.249	32.5	0.0032	
				Mean	0.0035	0.010
1 Per cent. solution of cellulose.						
34.6	0.841	21.4	0.761	3.4	0.0225	
34.4	"	9.6	0.627	9.9	0.0217	
33.0	0.836	3.7	0.472	16.6	0.0219	
34.2	0.837	1.5	0.319	27.7	0.0186	
				Mean	0.0212	0.025

The viscosity values show that the addition of a small amount of air brings about a great change, whilst further additions produce little effect. When, however, the content of the hypothetical cellulose "A" is considered, the effect of the air is, for cellulose of the same viscosity, roughly proportional to the amount added.

As was mentioned in Part I of this paper, oxygen reacts somewhat slowly with cuprammonium solution and produces nitrite, but it was proved during the present work that it is not the oxygen which so reacts which reduces the viscosity of cellulose, but that the reaction is direct. From the relative speeds of the two reac-

tions it would seem that most of the oxygen, when introduced into a cuprammonium solution, reacts with the cellulose.

From the above figures it is possible to calculate roughly the amount of oxygen necessary to reduce the viscosity of cellulose to its lowest limit, in other words, to convert all the cellulose "A" to cellulose "B." This amounts to about 5.3 c.c. per gram at *N.T.P.*, which means that 16 grams of oxygen react with about 2100 grams of cellulose. It will be seen that a similar figure is obtained in the experiments with sodium hypochlorite.

#### *Experiments on Undissolved Cellulose.*

It was noticed that the lowering of the viscosity of cellulose during the kierung operation was in general considerably greater than would have been expected from the results of autoclave experiments carried out under the same conditions of temperature and concentration of sodium hydroxide. The cause of this was found to be the air in the cotton, for when the cotton was thoroughly wetted and steamed before the caustic soda was added the cleaned cellulose had a much higher viscosity than that measured when no such precautions had been taken.

It was found that by simply boiling cellulose with 4 per cent. caustic soda for three-quarters of an hour at atmospheric pressure, during which time hydrogen peroxide was added, the viscosity was reduced from 2160 to 1.7 seconds. The cellulose had no copper reduction number and therefore it was evident that by this means the viscosity of cellulose could be lowered without the cellulose being appreciably degraded.

Experiments were then made using sodium hypochlorite instead of hydrogen peroxide. It is known that in acid solution cellulose is quickly attacked by chlorine ("Cellulose," 1918 edition, Cross and Bevan, p. 59). It was found that, when boiled with 4 per cent. sodium hydroxide and much hypochlorite, cellulose was rapidly disintegrated to a powder of very low viscosity. On further boiling, the powder became finer, and on being washed with water, swelled up. The powder was partly soluble in water, but was reprecipitated by sodium sulphate solution. It was noticed that during this boiling a yellow colour would suddenly appear; this indicated that all the hypochlorite had been used up, for the colour vanished on the addition of more of the reagent. By this means it was possible to oxidise cellulose almost entirely to carbon dioxide. When sugar was employed instead of cellulose, the same phenomenon was observed, and when the yellow colour appeared formaldehyde was detected by its odour.

It was found that by the addition of about 1.5 c.c. of *N*-sodium

hypochlorite per gram of cellulose the viscosity could be so reduced that a 4 per cent. solution had a viscosity of four seconds. When sodium carbonate solution was employed instead of sodium hydroxide, 0.8 c.c. of *N*-solution reduced the viscosity of a 4 per cent. solution to two and a half seconds. In the first instance substances soluble in sodium hydroxide would be formed which would react quickly with the hypochlorite, whilst with sodium carbonate solution all the oxygen of the hypochlorite would be used in lowering the viscosity. In these experiments, about 16 grams of oxygen reacted with about 2500 grams of cellulose. There was no chlorate formation in these reactions. The amount of oxygen consumed is of the same order of magnitude as that used in the reduction of the viscosity of cellulose in cuprammonium solution by gaseous oxygen. This means that the minimum molecular weight of cellulose must be at least 2500, should one atom of oxygen react with one molecule of cellulose.

Ultramicroscopic examination\* to determine whether the reduction in the viscosity is accompanied by an increase in the number of colloid particles yielded only negative results on account of the deep colour of the cuprammonium solution and the large amount of hydration which took place when other solvents were used.

The above work was carried out in the Research Department of Messrs. Nobel Industries Ltd., and the author has to thank Messrs. Nobel and Mr. William Rintoul, O.B.E., F.I.C., for permission to publish this paper. He also wishes to thank Mr. J. J. Fidd, who carried out many of the experiments described herein.

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### CCXC.—*The Sorption of Saturated Vapours by Charcoal.*

By JOHN DRIVER and JAMES BRIERLEY FIRTH.

In a previous paper (T., 1921, **119**, 1126), the authors showed that the sorption of alcohol by animal charcoal, when it is exposed to the saturated vapour, is about five times as great as the sorption of water for a given specimen of animal charcoal. Further, it was shown that in the case of mixtures of alcohol and water the alcohol is preferentially sorbed.

\* Carried out at Bristol University through the kind permission of Professor Francis Francis and Professor J. W. McBain.

In the present communication, the experiments have been extended to include other liquids and charcoals. The object of the first series of experiments was to determine the sorption of different liquids by a given specimen of animal charcoal. The second series had for its primary object the investigation of the sorption of certain liquids by different charcoals. A third series of experiments was carried out to determine the influence of heat on the activity of charcoal relative to the sorption of liquids.

### EXPERIMENTAL.

#### (1) Sorption of Liquids by Animal Charcoal.

The animal charcoal employed was a portion of the purified sample used in the previous experiments with alcohol and water (*loc. cit.*). The liquids were carefully dried and distilled several times before use; the first and the last runnings were rejected. The densities of the respective liquids at 25° ( $d_{25}^{25}$ ) were as follow :

Methyl benzoate .....	1.0773	Ethyl propionate .....	0.8877
Carbon tetrachloride .....	1.5730	Ethyl ether .....	0.7190
Chloroform .....	1.4761	Carbon disulphide .....	1.2903
Benzene .....	0.8732	Toluene .....	0.8639

The apparatus and the experimental procedure were exactly as described in the previous communication (*loc. cit.*). The results are given in the following table, where  $m$  is the weight of charcoal used and  $x$  the c.c. of liquid sorbed.

TABLE I.

Methyl benzoate. $m = 0.7350$ gram.			Ethyl propionate. $m = 0.7882$ gram.		
Time (days).	$x$ .	$x/m$ .	Time.	$x$ .	$x/m$ .
1	0.00474	0.006449	4 hours	0.007436	0.009436
2	0.00993	0.01351	2 days	0.02952	0.03745
3	0.01328	0.01807	5 "	0.06355	0.08063
6	0.02106	0.02865	9 "	0.08631	0.1070
8	0.02423	0.03296	11 "	0.10276	0.1303
13	0.03350	0.04422	20 "	0.15549	0.1972
16	0.03815	0.05090	26 "	0.18952	0.2405
20	0.05261	0.07158	80 "	0.37663	0.4775
29	0.06542	0.08900	90 "	0.39420	0.5001
35	0.08500	0.1155	110 "	0.4253	0.5396
108	0.29166	0.3968	131 "	0.4502	0.5712
134	0.33082	0.4397	150 "	0.4823	0.6119
141	0.34802	0.4735	160 "	0.4825	0.6120
145	0.3511	0.4776	165 "	0.4824	0.6120
160	0.3582	0.4873			
180	0.3961	0.5434			
200	0.4037	0.5493			
205	0.4038	0.5494			

THE SORPTION OF SATURATED VAPOURS BY CHARCOAL. 2411

TABLE I. (continued).

Chloroform.			Benzene.		
$m = 1.0876$ grams.			$m = 0.9284$ gram.		
Time.	$x$ .	$x/m$ .	Time (days).	$x$ .	$x/m$ .
10 mins.	0.2014	0.1852	1	0.0976	0.1052
20 "	0.2298	0.2113	2	0.1636	0.1762
1 hour	0.3560	0.3273	4	0.2312	0.2491
2 hours	0.4338	0.3988	6	0.2166	0.2280
3 "	0.4841	0.4410	8	0.3215	0.3416
1 day	0.6482	0.5961	12	0.3522	0.3793
4 days	0.6722	0.6180	15	0.3731	0.4019
6 "	0.6821	0.6272	20	0.3975	0.4282
10 "	0.6977	0.6413	25	0.4198	0.4522
14 "	0.7103	0.6531	35	0.4201	0.4525
16 "	0.7103	0.6531	65	0.4202	0.4526

Ethyl ether.			Toluene.		
$m = 1.1245$ grams.			$m = 1.0018$ grams.		
Time.	$x$ .	$x/m$ .	Time (days).	$x$ .	$x/m$ .
5 mins.	0.3132	0.2785	1	0.0813	0.08035
10 "	0.4214	0.3748	2	0.1153	0.1140
15 "	0.4956	0.4389	3	0.1502	0.1485
30 "	0.5163	0.4592	4	0.1823	0.1802
1 hour	0.5281	0.4697	6	0.2536	0.2506
2 hours	0.5192	0.4618	8	0.2611	0.2583
14 "	0.5104	0.4539	10	0.2823	0.2790
24 "	0.5003	0.4450	14	0.3238	0.3200
48 "	0.5000	0.4447	18	0.3571	0.3530
72 "	0.4998	0.4446	25	0.4010	0.3963
96 "	0.4999	0.4446	30	0.4112	0.4063
			36	0.4220	0.4171
			48	0.4221	0.4172

Carbon tetrachloride.			Carbon disulphide.		
$m = 0.6452$ gram.			$m = 0.6491$ gram.		
Time.	$x$ .	$x/m$ .	Time.	$x$ .	$x/m$ .
4½ hours	0.09687	0.1502	5 mins.	0.30309	0.4667
21 "	0.30151	0.4673	20 "	0.48944	0.7534
100 "	0.42245	0.6548	160 "	0.52325	0.8061
124 "	0.43359	0.6720	25 hours	0.45992	0.7086
61 "	0.43358	0.6720	72 "	0.44373	0.6836
			144 "	0.44373	0.6836

(2) Sorption of Liquids by Various Charcoals.

A second series of experiments was carried out in which different charcoals were employed. The charcoals were, lampblack, blood charcoal, sugar charcoal, cocoa-nut charcoal from the shell, cocoa-nut charcoal from the fruit. The cocoa-nut charcoal from the white tissue and from the shell were prepared by carbonisation at as low a temperature as possible. The blood charcoal gave initially 9.31 per cent. of ash, which diminished to 4.21 per cent. after repeated digestion with concentrated hydrochloric acid and

boiling for eight hours with distilled water. The cocoa-nut charcoal from fruit as prepared gave 21.30 per cent. of ash, and that from shell 1.21 per cent.; after purification as above, the ash was 3.98 and 0.371 per cent., respectively. The lampblack and the sugar charcoal, after purification, contained less than 0.1 per cent of ash. In the following table the time required for equilibrium and the value of  $x/m$  at equilibrium are given.

TABLE II.

Charcoal.	Water.		Chloroform.		Benzene.		Alcohol.	
	Time in days.	$x/m$ .	Time in days.	$x/m$ .	Time in days.	$x/m$ .	Time in days.	$x/m$ .
Lampblack .....	33	0.3842	19	0.9361	22	0.6992	23	0.8751
Blood charcoal .....	42	0.2649	23	0.8362	23	0.6410	28	0.7436
Sugar charcoal .....	51	0.1214	31	0.4212	31	0.3851	28	0.4016
Cocoa-nut charcoal								
from shell .....	53	0.0513	60	0.2235	54	0.1714	38	0.1236
Cocoa-nut charcoal								
from fruit .....	54	0.0936	47	0.3961	42	0.2107	41	0.4104

(3) *The Influence of Heat on the Activity of the Charcoal.*

It has previously been shown by one of us (Firth, T., 1921, **119**, 927) that the activity and the sorptive capacity of the charcoal, with regard to the sorption of gases, are greatly influenced by its previous heat treatment. A similar series of experiments has been carried out with liquids. The charcoals were heated in a vacuum at different temperatures for periods varying from six to forty-eight hours, the temperature being approximately determined by means of a pyrometer. The charcoal was allowed to cool in the vacuum and transferred as quickly as possible to the sorption apparatus. The results obtained are given in Table III. The two liquids used were chloroform and benzene, and the results are given in columns (a) and (b), respectively, in the table.

*Discussion of Results.*

The results in Table I show that the rate of sorption varies considerably with the different liquids, equilibrium being attained most rapidly in the cases of ether and carbon disulphide and exceptionally slowly with methyl benzoate and ethyl propionate.

The results given in Table II show that for a given liquid the volume sorbed for 1 gram of charcoal varies over a very wide range with the various charcoals used. In the case of lampblack, which was the most efficient charcoal used, the value varies from 0.3842 c.c. in the case of water to 0.9361 c.c. in the case of chloroform; with cocoa-nut shell charcoal, the values are 0.0513 c.c. and 0.2235 c.c., respectively. Again, the time required for equilibrium to be

TABLE III.  
 $\alpha$  = Chloroform.  $b$  = Benzene.

Charcoal heated to 600°.										Charcoal heated to 800°.										Charcoal heated to 1000—1100°.									
Period of heating in hours.	Time in days for equilibrium.				$x/m$ .		Time in days for equilibrium.				$x/m$ .		Time in days for equilibrium.				$x/m$ .		Time in days for equilibrium.				$x/m$ .						
	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).	(a).	(b).							
Animal charcoal	6	16	24	0.6672	0.4539	0.6672	0.4539	14	20	0.8972	0.6897	17	21	0.8902	0.6904	17	21	0.8902	0.6904	17	21	0.8902	0.6904						
	12	13	20	0.7211	0.5371	0.7211	0.5371	11	16	0.9354	0.7138	14	17	0.8901	0.6851	14	17	0.8901	0.6851	14	17	0.8901	0.6851						
	24	12	17	0.8036	0.6382	0.8036	0.6382	11	14	0.9698	0.7610	14	15	0.8720	0.6621	14	15	0.8720	0.6621	14	15	0.8720	0.6621						
	48	11	16	0.9012	0.7019	0.9012	0.7019	9	13	0.9863	0.7714	13	14	0.7963	0.6010	13	14	0.7963	0.6010	13	14	0.7963	0.6010						
Sugar charcoal	6	28	29	0.4310	0.3921	0.4310	0.3921	22	24	0.5492	0.5146	22	23	0.5938	0.4936	22	23	0.5938	0.4936	22	23	0.5938	0.4936						
	12	21	24	0.4721	0.4454	0.4721	0.4454	17	21	0.5998	0.5297	18	22	0.5792	0.4798	18	22	0.5792	0.4798	18	22	0.5792	0.4798						
	24	18	20	0.5639	0.4962	0.5639	0.4962	15	16	0.6105	0.5396	17	20	0.5801	0.4784	17	20	0.5801	0.4784	17	20	0.5801	0.4784						
	48	18	19	0.6031	0.5367	0.6031	0.5367	14	14	0.6263	0.5437	17	21	0.5620	0.4602	17	21	0.5620	0.4602	17	21	0.5620	0.4602						
Lamp-black	6	19	22	0.9299	0.7101	0.9299	0.7101	15	19	1.0436	0.8369	14	20	0.9853	0.8098	14	20	0.9853	0.8098	14	20	0.9853	0.8098						
	12	15	19	1.1042	0.7729	1.1042	0.7729	12	15	1.1984	0.8015	12	16	0.9965	0.8087	12	16	0.9965	0.8087	12	16	0.9965	0.8087						
	24	11	17	1.2136	0.8314	1.2136	0.8314	10	10	1.2513	0.8801	11	12	0.9402	0.7823	11	12	0.9402	0.7823	11	12	0.9402	0.7823						
	48	10	13	1.2542	0.8763	1.2542	0.8763	9	9	1.2602	0.8903	10	11	0.8710	0.7510	10	11	0.8710	0.7510	10	11	0.8710	0.7510						



attained is much less with lampblack than with cocoa-nut shell charcoal. From the results given in Table III it is again apparent that not only the activity but also the sorptive capacity is materially affected by heat treatment. In the cases given, heating at 900° for forty-eight hours results in an increased sorption of approximately 100 per cent. When the charcoals are heated rapidly to temperatures above 1000°, their sorptive capacities show a diminution; this, however, cannot be regarded as a diminution in the activity of the charcoal as a whole, but is the result of the conversion of a portion of the charcoal into a dense and more compact form of low sorptive power, and also possibly to the formation of a more stable crystalline phase. Hence the quantity of really active charcoal is less than the total charcoal, the actual amount diminishing with increase of period of heating (compare Firth, T., 1921, 119, 929).

The results cannot be considered to support the view of Gurvitsch (*J. Russ. Phys. Chem. Soc.*, 1915, 47, 805) that the volumes of liquid adsorbed vary over a relatively small range from 0.61 to 0.684 c.c. per gram of sorbing substance. Yet it would appear from Table I that under certain conditions a number of liquids may fall within this range; on the other hand, many fall outside it. Again, the results show that the sorptive capacity of a given charcoal for a given liquid can be varied over a wide range; hence any particular result falling within the range given by Gurvitsch must be regarded as a coincidence. It has been shown that, for the several charcoals used, the sorptive capacity for a given liquid varies considerably; which is in further disagreement with the general conclusion of Gurvitsch.

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## CCXCI.—Attempts to Prepare Red Sulphide Dyes. Part II. Mercaptan Derivatives of Azo-dyes.

By EDWIN ROY WATSON and SIKHIBHUSHAN DUTT.

MERCAPTAN derivatives of azo-dyes had already been prepared with the idea of using them as sulphide dyes (*vide* Friedländer and Mauthner, *Z. Farb. Ind.*, 3, 333; Müller, *ibid.*, 5, 357; D.R.P. 161462; Fichter, Fröhlich, and Jalon, *Ber.*, 1907, 40, 4420); but none of them were entirely satisfactory, either because they were insufficiently soluble in sodium sulphide or not easily oxidised on the fibre or the dyeings were not sufficiently fast to all agencies.

Despite these unsatisfactory results, it was thought worth while to prepare some more mercaptan derivatives of azo-dyes, especially as none had been prepared containing mercaptan groups (a) in the *o*-position to the azo-linking, (b) in naphthalene nuclei, or (c) on both sides of the azo-linking.

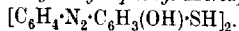
The following mercaptans and azo-mercaptans have now been prepared :

*m*-Hydroxyphenyl Mercaptan,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SH}$ .—*m*-Aminophenol (5.45 grams) was diazotised, the solution almost neutralised, and gradually poured into 16 grams of potassium xanthate in 50 c.c. of water kept at  $70^\circ$ . The oily product which separated was boiled with alcoholic sodium hydroxide for seven hours, the alcohol removed, and the residue dissolved in water and boiled with 20 c.c. of concentrated hydrochloric acid and 6.5 grams of zinc dust for an hour. After a second similar treatment with zinc dust and acid, the solution was cooled, extracted with ether, the filtered ethereal solution evaporated down, the residue dissolved in alcohol and treated with an alcoholic solution of 9 grams of lead acetate. The bright yellow precipitate obtained was filtered off, washed with alcohol, suspended in alcohol, and treated with excess of hydrogen sulphide. After filtering from lead sulphide, the alcohol was evaporated and pure *m*-hydroxyphenyl mercaptan (2.7 grams) was left as a yellow oil, soluble in caustic soda and giving an intense yellow colour with benzenediazonium chloride (Found :  $\text{S} = 24.9$ .  $\text{C}_6\text{H}_7\text{OS}$  requires  $\text{S} = 25.4$  per cent.).

Further experience showed that the treatment with lead acetate, etc., was unnecessary.

*Di*-*m*-hydroxyphenyl Disulphide,  $(\text{OH}\cdot\text{C}_6\text{H}_4)_2\text{S}_2$ .—The above mercaptan, dissolved in alcohol, was treated with excess of ferric chloride in alcoholic solution. The oil precipitated on addition of water solidified when washed by decantation. It was recrystallised from boiling water and obtained as white, hexagonal plates melting at  $85\text{--}90^\circ$  (Found :  $\text{S} = 25.4$ .  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}_2$  requires  $\text{S} = 25.6$  per cent.).

*Diphenyl*-4 : 4'-bisazohydroxy-2-phenyl Mercaptan,



—Benzidine (3.72 grams) was diazotised and coupled with 5.4 grams of *m*-hydroxyphenyl mercaptan in alkaline solution. After standing over-night, the mixture was acidified and boiled and the dye filtered off. It is soluble in sodium sulphide and dyes cotton red, but the colour changes to brownish-yellow on oxidation in air. The dyeings possess considerable fastness, but are not so fast to alkalis as dyeings with ordinary yellow sulphide dyes (Found :  $\text{S} = 13.5$ .  $\text{C}_{12}\text{H}_9\text{ON}_2\text{S}$  requires  $\text{S} = 13.97$  per cent.).

*1-Hydroxy-5-naphthyl Mercaptan*,  $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{SH}$ .—A bright orange-yellow solution and a brown precipitate were obtained when 5-amino-1-naphthol (8.8 grams) was diazotised. The precipitate (1.7 grams) was washed with ice-cold water, the filtrate and washings were mixed and poured into a cold solution of 13.2 grams of potassium xanthate in a little water, and the mixture was heated at  $75^\circ$  for half an hour. The oil which separated was dissolved in ether, the filtered solution evaporated, and the residue boiled for six hours with a solution of 17.6 grams of sodium hydroxide in 110 c.c. of alcohol. The alcohol having been removed, the residue was dissolved in water and acidified, when a dark-coloured oil was precipitated. The mixture was boiled with two successive doses of zinc dust and hydrochloric acid, when the oil became lighter in colour and, on cooling, solidified, whilst the aqueous liquid was filled with white crystals. The solid was purified by treatment with lead acetate and hydrogen sulphide as in the case of *m*-hydroxyphenyl mercaptan and there were obtained 2 grams of a white, crystalline substance softening at  $105^\circ$  and melting at  $115^\circ$  (Found:  $\text{S} = 19.8$ .  $\text{C}_{10}\text{H}_7\text{OS}$  requires  $\text{S} = 18.8$  per cent.).

*1:1'-Dihydroxy-5:5'-dinaphthyl Disulphide*,  $(\text{OH}\cdot\text{C}_{10}\text{H}_7)_2\text{S}_2$ .—Prepared from the preceding compound by means of alcoholic ferric chloride solution, and precipitated by water, the *disulphide* was obtained in white crystals melting at  $190$ – $200^\circ$  (Found:  $\text{S} = 19.45$ .  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}_2$  requires  $\text{S} = 18.3$  per cent.).

*Diphenylbisazo-1-hydroxy-5-naphthyl Mercaptan*,  
 $[\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7(\text{OH})\cdot\text{SH}]_2$ .

—Benzidine was diazotised in the usual way and coupled with 1-hydroxy-5-naphthyl mercaptan (2 mols.) in presence of caustic soda (4 mols.). The mixture was left over-night, the dyestuff salted out, and dried on porcelain.

It was used in this condition for dyeing tests. For analysis, it was dissolved in water, precipitated with hydrochloric acid, boiled, filtered, washed, and dried (Found:  $\text{S} = 10.9$ .  $\text{C}_{32}\text{H}_{22}\text{O}_2\text{N}_4\text{S}_2$  requires  $\text{S} = 11.47$  per cent.).

The dyestuff is only slightly soluble in sodium sulphide and does not give good dyeings on cotton from a sulphide bath.

*2-Hydroxy-7-naphthyl mercaptan*,  $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{SH}$ , prepared from 7-amino-2-naphthol (4 grams) in the same way as 1-hydroxy-5-naphthyl mercaptan from the corresponding aminonaphthol, was obtained as an oil which became solid on keeping and melted at  $60$ – $70^\circ$  (yield 0.6 gram) (Found:  $\text{S} = 19.4$ ,  $17.6$ .  $\text{C}_{10}\text{H}_7\text{OS}$  requires  $\text{S} = 18.18$  per cent.).

*Diphenylbisazo-2-hydroxy-7-naphthyl mercaptan*  
 $[\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7(\text{OH})\cdot\text{SH}]_2$ .

was prepared in exactly the same way as the corresponding derivative of 1-hydroxy-5-naphthyl mercaptan (Found:  $S = 10.7$ .  $C_{32}H_{22}O_2N_4S_2$  requires  $S = 11.47$  per cent.). It is almost insoluble in sodium sulphide.

*Diphenylbisazo-2-hydroxy-7-naphthyl Xanthate,*  
 $[C_6H_4 \cdot N_2 \cdot C_{10}H_6(OH) \cdot S \cdot CS \cdot OEt]_2$ .

—Benzidine was diazotised and coupled in the usual way with 1-hydroxy-5-naphthyl xanthate (2 mols.) in presence of sodium hydroxide. The hydroxy-xanthate was finely powdered and rubbed with cold sodium hydroxide solution. Warming was avoided, as it was found to make the solution turbid. On coupling, a purple precipitate was obtained. More sodium hydroxide (6 mols. altogether) was added, the mixture left over-night, and the dyestuff salted out. For analysis, it was boiled with dilute hydrochloric acid, filtered, washed, and dried (Found:  $S = 18.3$ .  $C_{19}H_{15}O_2N_2S_2$  requires  $S = 17.44$  per cent.).

The substance is soluble in sodium sulphide and dyes dull maroon shades on cotton, but the affinity for cotton is not great.

Experiments on the hydrolysis of this compound for the preparation of the corresponding mercaptan dyestuff were not very successful.

*3-Nitro-4-thiolbenzenazo-4-hydroxy-2-phenyl Mercaptan,*  
 $NO_2 \cdot C_6H_3(SH) \cdot N_2 \cdot C_6H_3(OH) \cdot SH$ .

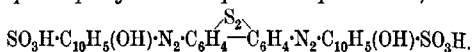
—The 2-nitro-4-amino-1-phenyl mercaptan required for the preparation was obtained crystalline with m. p.  $216^\circ$  (according to the literature,  $222^\circ$ ). This substance (4.2 grams) was rubbed up with 7 c.c. of concentrated hydrochloric acid and mixed with 60 c.c. of ice-cold water. Sodium nitrite (2 grams, dissolved in a little water) was then gradually added. A clear solution not being obtained during about half an hour, the mixture was poured into a cold solution of 3.2 grams of *m*-hydroxyphenyl mercaptan in 125 c.c. of 2 per cent. caustic soda solution, when a dark orange-brown solution was formed. After remaining for half an hour, it was acidified with hydrochloric acid, and the precipitated dyestuff filtered off, washed, and dried (Found:  $S = 21.2$ ;  $N = 13.3$ .  $C_{12}H_9O_3N_3S$  requires  $S = 20.85$ ;  $N = 13.68$  per cent.).

The dyestuff is soluble in sodium sulphide and gives fairly good brown shades on cotton from a sulphide bath.

*Benzenazo-thioresorcinol*,  $C_6H_3 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot SH$ .—A portion of the sample of thioresorcinol used in Part I of this investigation [analysis agreeing with the formula  $C_6H_3(OH)_2 \cdot S_{1.03}H$ ] was dissolved in caustic soda and coupled with benzenediazonium chloride. The dyestuff was salted out, collected, and acidified with hydrochloric acid (Found:  $S = 15.0$ ; calculated from the percentage

of sulphur in sample of thioresorcinol used, S = 14.47 per cent.) It dyes cotton yellowish-brown from a sulphide bath.

*Disulphidodiphenylbisazo- $\alpha$ -naphthol-2-sulphonic Acid,*



—The thiobenzidine used in this and other experiments was prepared by heating a mixture of 5.1 grams of benzidine (1 mol.) and 3.2 grams of sulphur (4 atoms) at 180–200° for twelve hours. The mixture melted and evolved hydrogen sulphide during the early stages of heating. The product was powdered and digested over-night with dilute hydrochloric acid (8 per cent.). On neutralisation with sodium hydroxide, the filtrate gave a yellow precipitate which was boiled several times with water to remove unchanged benzidine. The product (3.2 grams) melted at 265–270° with decomposition (and therefore was different from the substance described in D.R.-P. 38795) (Found: S = 20.1.  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_{1.43}$  requires S = 20.1 per cent.).

Thiobenzidine (0.492 gram), dissolved in 3 c.c. of concentrated hydrochloric acid and a little hot water and diluted to 28 c.c. with more water, remained in solution on cooling. The ice-cold solution was diazotised with 4 c.c. of *N*-sodium nitrite, the mixture (containing an orange-coloured precipitate) coupled with Schäffer's salt in soda solution (in excess of 2 mols.), and the dyestuff isolated in the usual way (Found: S = 15.2.  $\text{C}_{32}\text{H}_{20}\text{O}_8\text{N}_4\text{S}_{3.43}$  requires S = 15.7 per cent.).

The dyestuff is crimson and dyes cotton directly (compare D.R.-P. 38795) and also from a sulphide bath. The dyeings are faster to alkali than most direct cotton dyes, but are not so good as ordinary sulphide dyes, a result to be expected from the presence of sulphonic acid groups.

Dyestuffs were also formed by coupling diazotised thiobenzidine with  $\beta$ -naphthol and di- $\alpha$ -naphthol trisulphide, but the products were not sufficiently pure for analysis, nor were they satisfactory red sulphide dyes.

*Di- $\alpha$ -naphthol Trisulphide,  $(\text{C}_{10}\text{H}_6\cdot\text{OH})_2\text{S}_3$ .*—A warm solution of  $\alpha$ -naphthol in aqueous caustic soda has the property (similar to that possessed by resorcinol and  $\beta$ -naphthol) of dissolving sulphur and forming a sulphide, which is precipitated by acid. By using 4 atoms of sulphur for each molecule of  $\alpha$ -naphthol, it was expected to obtain a polysulphide approximating to the formula  $(\text{C}_{10}\text{H}_6\cdot\text{OH})_2\text{S}_7$ , but its composition agreed closely with the formula  $(\text{C}_{10}\text{H}_6\cdot\text{OH})_2\text{S}_3$ . It showed a tendency to crystallise (Found: S = 25.1.  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}_3$  requires S = 25.1 per cent.).

*Diphenylbisazodi- $\alpha$ -naphthol Trisulphide,  $[\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})]_2\text{S}_3$ .*

—Benzidine was diazotised in the usual way and coupled with excess of di- $\alpha$ -naphthol trisulphide in caustic soda solution. After keeping over-night, the dyestuff was salted out. For analysis, it was dissolved in water and precipitated by hydrochloric acid (Found: S = 16.7.  $C_{32}H_{20}O_2N_4S_3$  requires S = 16.3 per cent.). It is soluble in caustic soda and in sodium sulphide, but dyes cotton only in light clay-coloured shades from a sulphide bath.

The substances described in the paper were first prepared in the British Dyes Laboratory at Leeds University and have been again prepared and analysed in the chemical laboratory at Dacca University. Our thanks are due to the British Dyestuffs Corporation, Ltd., for permission to publish these results.

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## CCXCII.—*The Form of the Vapour Pressure Curve at High Temperature. Part I. The Curve for Lead.*

By CHRISTOPHER KELK INGOLD.

THE various vapour pressure formulæ which have been proposed from time to time have hitherto been tested on substances the boiling points of which embrace a somewhat limited range of temperature, and it is obviously of great importance in connexion with the general theory of the continuity of the fluid state of matter that measurements of vapour pressure should be continued as far as possible into the regions of very low and very high temperature. None of the vapour pressure formulæ which at present hold the field has an entirely satisfactory theoretical basis, and it is undoubtedly true that they are retained principally by virtue of their accuracy in expressing experimental data over the comparatively limited ranges of temperature to which they have been applied. Evidently, therefore, a more searching test is necessary, and it is by examining the applicability of vapour pressure formulæ under extreme conditions of temperature that we may expect to see them in their true perspective, to isolate partly compensating or superimposed discrepancies, and to determine in how far these are to be traced to known inadequacies of theoretical foundation.

With these objects in mind, we may proceed to consider first of all, in the light of the vapour pressure formulæ of Kirchhoff, Hertz, and Nernst, the numerical results contained in the experimental



near the ordinary temperature,  $v$  is usually of the order of 1000 times  $v'$ , but for liquids boiling at 1000–1500° the ratio must be nearer 5000, and still greater at diminished pressures. Obviously, therefore, there is no need to consider assumption (b) as a possible source of inaccuracy.

The same is not necessarily true, however, of the assumptions (a) and (c), or even of the second approximation (c'). It would be of great interest to know what form the vapour pressure equation would assume if one were to combine the thermodynamic equation (i) with Berthelot's or Dieterici's equation of state, but, unfortunately, the expression so obtained cannot be integrated. On general grounds, however, it is obvious that errors due to deviations of the saturated vapour from the gas laws must become more noticeable at high pressures, and it would be reasonable to attribute divergences of this character to the inapplicability of the gas laws, provided that it could be shown that the errors involved in assumptions (c) or (c') are small.

It was for this reason that lead was chosen as the subject of the present investigation. It was necessary in the first place that the liquid used should have an ordinary boiling point of about 1400–1600°, that is, above, but not too much above, the highest temperature that could be reached and measured with the apparatus used. Secondly, it was desired that the liquid should give a monatomic vapour.

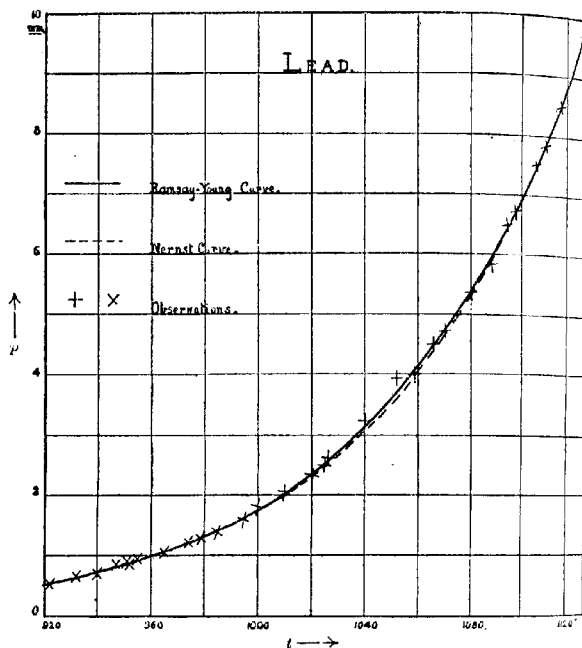
The boiling point of lead has been estimated by Greenwood (*Z. Elektrochem.*, 1912, **18**, 319) as 1525° or 1570°, and by Wartenburg as 1630° (*ibid.*, 1913, **19**, 484). The vapour density of lead has been determined by Wartenburg (*Z. anorg. Chem.*, 1908, **56**, 320), who obtained the normal value. According to the kinetic theory, the specific heats of all monatomic gases are invariant with temperature, and this conclusion is fully supported as regards argon by Pier's measurements extending to 2350° (*Z. Elektrochem.*, 1909, **15**, 538). For a monatomic gas, then,  $C_p$  is constant, and one of the factors which contribute to the departure from the straight-line laws of the relationship between  $\lambda$  and  $T$  is therefore eliminated. If one could be certain that there was no association in the liquid state,  $C_p$  would also be constant, and there would be no need for the term  $\beta T$  in equation (iii). We could then regard the Kirchhoff-Hertz equation as expressing the vapour pressure to the same degree of accuracy as that to which the gas laws apply to the saturated vapour. Such an assumption, however, is unwarranted; but, on the other hand, there is every reason to believe that the specific heats of liquid metals vary very little with temperature, and that the small variations which do occur can



accurately be expressed as linear relationships.\* Evidently, then, it is necessary to employ equation (iii); but in the case of liquid metals at least, we may be fairly certain that it is sufficiently comprehensive to include all deviations from the simpler relationship other than those due to departures from the gas laws.

The method of testing the equation was as follows. The whole experimental range of temperature was divided into two equal

FIG. 1.



portions, 920—1130° and 1130—1340°, and the observations in each interval were plotted on squared paper (Figs. 1 and 2). Smooth curves were drawn through each set of points, and from one of them (Fig. 1) four values were selected by means of which a formula of type (iii) could be calculated. The four values were ( $t = 921^\circ$ ,  $p = 0.50$  mm.), ( $t = 963^\circ$ ,  $p = 1.00$  mm.), ( $t = 1075^\circ$ ,  $p = 5.00$  mm.),

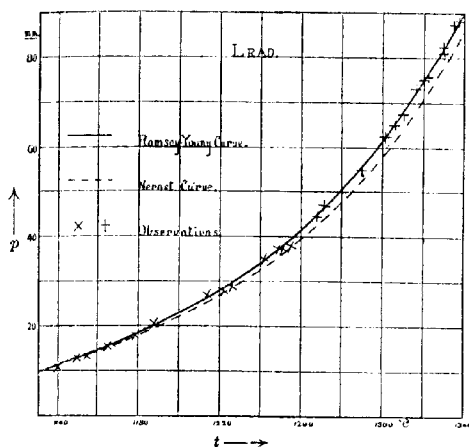
\* This is known to be so in the case of mercury, for which Mithaler gives the formula  $C = 0.033266 - 0.0000092 t$  between  $0^\circ$  and  $200^\circ$  (Wied. *Annalen*, 1899, 36, 897).

and ( $t = 1129^\circ$ ,  $p = 10.0$  mm.), and the formula to which they led was

$$\log_{10} p = 4.818 - \frac{11160}{T} + 1.750 \log_{10} T - 0.000982 T. \quad (\text{iv})$$

(where  $T = t + 273$  and  $p$  is reckoned in mm. of mercury). The graph of this equation was now plotted on each of the diagrams of experimental observations. In the first temperature interval,  $920$ — $1130^\circ$ , it was found to fit closely over the experimental curve, as, indeed, was to be expected. This agreement is such that the

FIG. 2.



two curves can only just be distinguished separately on the scale to which Fig. 1 is drawn. In the second range of temperature, however, the theoretical and experimental curves diverge more and more as the pressure rises, the difference between them amounting to  $6^\circ$  or about 4 mm. pressure (Fig. 2) in the neighbourhood of  $1300^\circ$ . Since the individual temperature measurements are believed to be accurate to  $1^\circ$  and the pressure readings to 0.1 mm. at this end of the series, there can be no question but that the observed discrepancy represents a defect of theory in the sense indicated above.

In order to be certain that this "extrapolation test" was not too sensitive to slight differences in the numerical constants, the whole process was repeated, the observations being plotted afresh and a new set of four values selected. The results were identical.

It is a remarkable fact that, although the experimental observy.

ations cannot adequately be represented by a formula of type (iii), they can be expressed with great accuracy by Ramsay and Young's empirical formula

$$T_1/T_2 = m + nT_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (v)$$

(where  $T_1$  and  $T_2$  are the absolute boiling points of two liquids under the same pressure, and  $m$  and  $n$  are constants,  $n$  being small), which satisfies an even more exacting extrapolation test than that used in connexion with formula (iv). The comparison liquid was mercury, and the values of its vapour pressure were taken from the table given by Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, 32, 1447). Two points ( $t = 94.4^\circ$ ,  $p = 0.76$  mm.) and ( $t = 106.0^\circ$ ,  $p = 4.18$  mm.), chosen to include approximately the first quarter of the whole experimental interval of temperature, gave the equation

$$T_{\text{Pb}}/T_{\text{Hg}} = 3.244 - 0.00038 T_{\text{Hg}} \quad . \quad . \quad . \quad (\text{vi})$$

by means of which the observations in the remaining three-quarters of the range could be expressed with an accuracy at least equal to that which the measurements themselves are believed to possess. The graph of equation (vi) lies so closely on the curve of smoothed experimental results that it is impossible to distinguish them on the scale to which the diagrams are constructed.

Henglein's formula,\*

$$\log T_1 = a \log T_0 + b \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{vii})$$

for which a theoretical basis has been claimed (Z. *Elektrochem.*, 1920, **26**, 431), was also examined. Using the lower half of the temperature range to obtain the constants, the formula

$$\log T_{\text{Pb}} = 0.953 \log T_{\text{Hg}} + 0.613 \quad . \quad . \quad . \quad . \quad (\text{viii})$$

was calculated and its graph constructed. The graph fitted well over the experimental curve in the temperature interval 930–1130°, but in the second interval, 1130–1340°, it diverged more and more at the higher temperature, approximating very closely to the curve for the Kirchhoff-Hertz-Nernst formula (iv). The correspondence does not continue, however, above the experimental range; at high temperatures the Henglein curve lies between the Kirchhoff-Hertz-Nernst curve and the Ramsay-Young curve, as is shown by the following calculations of the boiling point of lead under atmospheric pressure :

\* Putting  $b = \log k$ , this may be written  $T_1 = kT_2^a = kT_2^{1+b}$ , where  $k$  is small, since  $a$  is always close to unity. If expanded, higher powers of  $k$  than the first being neglected, this becomes  $T_1 = kT_2(1 + b \log_e T_2)$ , that is,

$$T_1/T_2 = k + h k \log_2 T_2$$

which shows its relationship with Ramsay and Young's equation,

	B. p. of lead.
Extrapolated by the Ramsay-Young formula (vi) .....	1619° } $\Delta = 18^\circ$
Extrapolated by the Henglein formula (viii) .....	1637° }
Extrapolated by the Nernst formula (iv) .....	1653° } $\Delta = 16^\circ$

Since the Ramsay-Young formula is the only one which fits the observations, we may conclude that the error in the calculated value, 1619°, for the boiling point is a good deal less than any of the differences between the three figures tabulated.\*

It is truly remarkable that the only one of the three formulæ investigated which accurately expresses the experimental results should be the only one with no claim to any theoretical foundation. The Ramsay-Young formula does not appear to have been tested previously on a pair of substances having such widely different boiling points as mercury and lead, and since over the intervals of temperature within which it has been employed other vapour pressure formulæ have represented the observations equally well, its extraordinary accuracy and range of application as a two-constant formula have not been sufficiently emphasised. Obviously, the whole matter hinges on the establishment of a general equation of state from which, with the aid of Maxwell's theorem of the isotherm, a vapour pressure formula can be derived which reduces to Ramsay and Young's formula when the variable  $p$  is eliminated between equations for two substances. None of the characteristic equations hitherto proposed fulfils this condition, although Henglein's calculations (*loc. cit.*) are certainly to be regarded as a first step in the required direction.

## EXPERIMENTAL.

### (A)—Purification of Materials.

**Lead.**—Kahlbaum's pure lead was distilled in quantities of about 10 grams in a small porcelain retort which, after introduction of the metal, was filled with pure nitrogen and then evacuated to a pressure of less than 0.05 mm. The heating was performed with an ordinary Bunsen burner. Head and tail fractions of about 2 grams each were rejected, and the middle fraction, which was

\* A rounded value,  $1620^\circ \pm 10^\circ$ , may perhaps be accepted provisionally. Wartenburg's estimate, b. p.  $1630^\circ \pm 20^\circ$  (*loc. cit.*), is in good agreement, but Greenwood's values are decidedly too low and do not agree amongst themselves (*loc. cit.*). However, Johnston (*J. Ind. Eng. Chem.*, 1917, **9**, 873) calculates b. p.  $1640^\circ$ , and Hildebrand, on the basis of his entropy rule, gives a formula (*J. Amer. Chem. Soc.*, 1918, **40**, 45) leading to the value  $1615^\circ$ . On the whole, therefore, the measurements herein recorded may be said to receive support from other sources.

Again, the observations lead to the value for the latent heat of vaporisation,  $\lambda = 47000$  cals., to two significant figures. Johnston calculates  $\lambda = 45400$ , and Hildebrand  $\lambda = 47500$  cals. (*loc. cit.*).

obtained as a button and some small beads of bright mercurial lustre, was examined as regards its melting point and density.

The melting points were taken with a platinum thermometer standardised by means of the b. p.'s of water ( $100^{\circ}$ ) and sulphur ( $445^{\circ}$ ). The extreme determinations were  $326.0^{\circ}$  and  $327.8^{\circ}$ ; specimens having m. p. above  $326.5^{\circ}$  were accepted as satisfactory. Density determinations varied from 11.325 to 11.345, but no otherwise satisfactory specimens were rejected on account of low density, as this may have been due to the inclusion of minute bubbles. Holborn and Day quote  $326.9^{\circ}$  as the m. p. (*Ann. Physik*, 1900, [iv], 2, 505), and Kahlbaum, Roth, and Siedler give 11.3470 as the density of metal which had been pressed under 10,000 atmospheres (*Z. anorg. Chem.*, 1902, 29, 278).

*Mercury.*—The mercury employed in the pressure gauge was distilled in a vacuum, washed with dilute nitric acid by Hildebrand's method (*J. Amer. Chem. Soc.*, 1909, 31, 933), and then tested in the manner recommended by Hulett and Minchin (*Physical Rev.*, 1905, 21, 388). The potential difference between the sample and a portion of it which had been distilled twice in air to oxidise metallic impurities, if present, could not be read on a galvanometer which would have detected 0.000005 volt.

*Nitrogen.*—The nitrogen employed was taken from a cylinder and purified by passage through three towers of pumice soaked in alkaline pyrogallate, two soda-lime tubes, three bulbs containing phosphoric oxide, and two additional bulbs, one empty and the other filled with cotton wool. These were intended as dust traps, but they did not appear to catch any dust and could probably have been dispensed with.

#### (B)—Apparatus.

*General.*—The vapour pressure measurements were made by an adaptation of the usual dynamic method, the lead being boiled under varying pressures of nitrogen in a tube, the upper portion of which served as a reflux condenser. A thermometer immersed in the vapour gave the temperature, whilst the pressure was read from a manometer attached to the cooler parts of the apparatus.

*Boiling-tubes.*—Several kinds of tubes were tried, but porcelain and carbon tubes were the only ones which gave consistent results and proved satisfactory in other respects. Some of the observations tabulated below were made with carbon tubes and others with porcelain tubes. The tubes were all about 36 cm. long and 2 cm. in internal diameter. The carbon tubes were turned from stout rods of the quality used for arc lamps; their life at the high temperature employed was rather short, and they were not entirely

gas-tight, as was shown by the presence of traces of carbon monoxide in the nitrogen pumped off; on the other hand, the metal boiled in them with absolute regularity and the temperature readings were thereby much facilitated.

*Furnace.*—An attempt to use a platinum resistance furnace was abandoned owing to the fact that heat could not be supplied quickly enough to maintain rapid ebullition.

The arrangement finally adopted was a gas-fired furnace constructed of specially shaped and trued silica bricks, which, when placed together and held in position by iron bands, left a spherical cavity, 10 cm. in diameter, having three cylindrical openings, 3 cm. in diameter, one at the bottom and two near the top. Heating was performed through the bottom opening by means of a water-cooled oxy-coal gas or oxy-hydrogen blowpipe. Through one of the upper openings the tube was inserted to such a depth that the boiling metal occupied the centre of the spherical cavity. The other opening, which could be partly or wholly covered by a brick, served to emit the flame gases.

In addition to this furnace, a subsidiary furnace was employed in order to heat the first 8 cm. of the projecting portion of the boiling-tube. This was a cylindrical electric furnace consisting of a platinum strip, bedded in burnt magnesium oxide and wound on a porcelain tube, 9 cm. long and 3 cm. in internal diameter, the whole being packed in asbestos. This furnace slipped easily over the boiling-tube and rested on the lid of the main furnace during an experiment.

The heat from these furnaces was prevented from reaching the upper end of the boiling-tube by surrounding the uppermost 12 cm. with a lead coil carrying cold water.

*Thermometer.*—Good results were obtained with a platinum resistance thermometer, but a platinum-rhodium thermocouple was found to be the most convenient instrument for the purpose. One wire passed through a silica capillary, and the whole could be slipped as far as necessary into the porcelain thermometer tube. The compactness and ease of mechanical adjustment of the thermocouple constituted its chief advantage over the resistance thermometer, especially in exploring the tube for variations of temperature.

The results tabulated below were all measured with the couple, which was standardised from 850° to 1400° by direct comparison in a fused sodium chloride bath with the platinum resistance thermometer, the fixed points of which were determined with reference to the melting points of sodium chloride (800°), copper (1083°, in a vacuum), and nickel (1452°). As a further check, the melting points of sodium chloride, sodium sulphate (884°), silver

(961°), potassium sulphate (1063°), copper, and nickel were determined by means of the couple, and were found to be correct to within one degree. The cold junctions were kept at 0° in all cases. The standardisation was repeated at frequent intervals, and, in particular, just before and just after the four final sets of readings recorded in section D.

*Manometer.*—This consisted of a glass tube, 1 cm. in internal diameter, dipping in a mercury cup with a screw adjustment by means of which the level could be set with the aid of an ivory pointer as in an ordinary barometer. The readings were made on a steel scale with a vernier and cursor attached to the same carriage, controlled by a milled wheel, a mirror at the back being used to eliminate parallax.

The readings, which, it is believed, were accurate to 0.05 mm., were corrected for capillarity, and for the thermal expansion of mercury and steel between 0° and the temperature of the instrument.

*Nitrogen Supply.*—Increases of pressure were effected by letting in nitrogen from a reservoir, consisting of a large test-tube inverted over mercury, in which it was stored as required. One section of the nitrogen supply tube was of capillary tubing, so that the quantity of gas which passed could be roughly regulated by opening the stop-cock for a definite length of time.

*Pumps.*—Reductions of pressure were effected by means of a two-stage Geryk oil pump backed by a water pump.

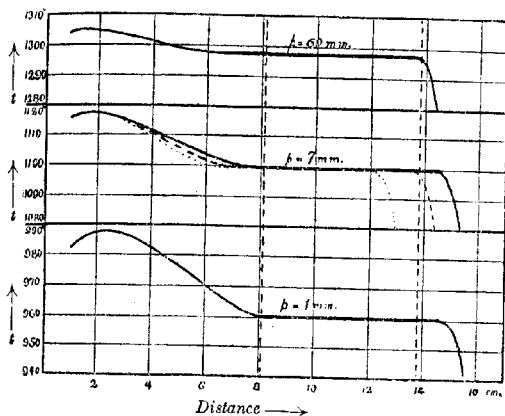
#### (C)—Preliminary Experiments.

By changing the distance of the thermocouple from the surface of the liquid it was found that, for moderate pressure (3 to 30 mm.) under the conditions used, there was a space, 6–9 cm. long, within which quite concordant readings of the temperature of the condensing vapour could be obtained. Below this region there was appreciable superheating; above it, the vapour evidently did not reach the thermocouple. The exact position of the region of constant temperature was found to depend to some extent on the pressure; thus, on reducing the pressure below 3 mm., the region moved noticeably higher up the tube, with the result that a thermocouple placed so that it recorded accurate boiling points for higher pressures suddenly ceased to give correct boiling points when the pressure was diminished below a certain limit.

A number of such quantitative experiments were made both without and with the use of the subsidiary furnace; and they showed that its use was necessary, and that it should be kept approximately 100° below the observed boiling point, in order that the thermocouple in a set position should always be within

the zone of true condensation without being subject either to splashing or to superheating. Fig. 3 shows typical distributions of temperature; and in the middle section are shown the distributions, for a pressure of 7 mm. (b. p.  $1100^{\circ}$ ), (a) without the subsidiary furnace (dotted curve), (b) with the subsidiary furnace at  $800^{\circ}$  (broken curve), and (c) with this furnace at  $1000^{\circ}$  (full-line curve). The actual readings are omitted from the diagram for the sake of clearness, but they were all within  $2^{\circ}$  of the appropriate curve. It will be seen by inspection of the three full-line curves on the diagram that the section of the tube between 8 and 14 cm. from the liquid surface always attains the temperature of the

FIG. 3.



condensing vapour over the whole range of pressures and temperatures examined.

The temperatures recorded in the experiment described below were usually taken near the middle of this interval, but occasionally near to one end or the other.

The temperature of the subsidiary furnace was measured optically through a small aperture provided for the purpose.

#### (D)—Final Experiments.

Although during the course of the preliminary experiments certain sections of the vapour pressure curve were traced fairly accurately, the figures recorded below are taken exclusively from four experiments in each of which the whole, or almost the whole, of the temperature range ( $920$ — $1340^{\circ}$ ) was traversed. The details of these experiments are as follow :



## 2430 INGOLD: THE FORM OF THE VAPOUR PRESSURE CURVE

(1) Porcelain tube. Readings taken in order of ascending pressures.

(2) Porcelain tube. Readings taken in order of descending pressures.

(3) Carbon tube. Readings taken in order of ascending pressures.

(4) Carbon tube. Readings taken in order of descending pressures.

In Table I, the first column contains the reference number of the experiment, and the second and third columns the observed pressures and temperatures. The temperatures calculated by the Ramsay-Young formula (vi) to correspond with the observed pressures are recorded in the fourth column, whilst the fifth shows the differences between the temperatures observed and calculated. The sum of the differences for all the fifty-eight observations is  $-1^\circ$ , so that the average difference is  $-0.016^\circ$ , or approximately zero, as it should be. On the other hand, the average of the differences for the first twenty-nine observations is  $-0.2^\circ$  and of the second twenty-nine readings is  $+0.2^\circ$ , so that the general agreement is evidently capable of being slightly improved by a small change in the constants of the formula, although it was not thought worth while to attempt any such refinement.

TABLE I.

No.	<i>p</i> (mm.).	<i>t</i> (°C.).	<i>t</i> (calc.).	$\Delta$ .	No.	<i>p</i> (mm.).	<i>t</i> (°C.).	<i>t</i> (calc.).	$\Delta$ .
3	0.50	922°	922°	0	1	9.75	1129°	1128°	+1
4	0.65	932	934	-2°	2	11.2	1140	1139	+1
2	0.70	940	939	+1	3	12.9	1150	1151	-1
1	0.85	947	949	-2	1	13.5	1155	1154	+1
3	0.85	952	949	+3	4	16.0	1165	1166	-1
1	0.90	951	953	-2	2	18.1	1179	1178	+1
2	0.95	955	957	-2	3	20.6	1188	1190	-2
4	1.05	965	965	0	4	26.0	1214	1216	-2
1	1.20	974	974	0	1	27.9	1222	1220	+2
3	1.30	979	979	0	3	29.0	1226	1223	+3
2	1.40	985	984	+1	2	35.1	1242	1243	-1
4	1.60	995	994	+1	1	37.5	1249	1250	-1
3	1.80	1000	1001	-1	4	37.5	1251	1250	+1
2	2.05	1010	1010	0	3	38.1	1255	1251	+4
4	2.35	1020	1020	0	2	44.4	1268	1267	+1
1	2.50	1025	1024	+1	1	46.9	1271	1273	-2
2	2.60	1026	1027	-1	4	50.0	1280	1280	0
4	3.25	1040	1042	-2	1	53.9	1287	1287	0
3	3.95	1052	1056	-4	3	55.0	1290	1289	+1
1	4.00	1059	1057	+2	2	62.6	1301	1301	0
4	4.50	1066	1066	0	3	65.0	1306	1306	0
3	4.75	1070	1070	0	4	67.4	1310	1309	+1
2	5.40	1080	1080	0	1	73.0	1316	1317	-1
3	5.85	1088	1087	+1	1	74.9	1320	1320	0
4	6.50	1094	1095	-1	3	75.7	1322	1321	+1
2	6.75	1098	1098	0	4	81.3	1330	1329	+1
1	7.50	1106	1106	0	3	82.6	1330	1330	0
3	7.85	1110	1110	0	4	87.5	1335	1337	-2
4	8.50	1117	1117	0	3	88.5	1338	1338	0

Table II gives the vapour pressure of lead in mm. of mercury for every  $10^\circ$  between  $920^\circ$  and  $1340^\circ$ . The first column contains the temperature, and the second the pressure, read from the curve of smoothed experimental results which is indistinguishable from the curve of the Ramsay-Young formula (vi). The third and fourth columns contain the pressures calculated by the Henglein formula (viii) and the Nernst formula (iv), respectively.

TABLE II.

$t$ (°C.).	$p$ -Obs., and calc. by vi. (mm.).	$p$ -Calc. by viii. (mm.).	$p$ -Calc. by iv. (mm.).	$t$ (°C.).	$p$ -Obs., and calc. by vi. (mm.).	$p$ -Calc. by viii. (mm.).	$p$ -Calc. by iv. (mm.).
920°	0.49	0.49	0.49	1140°	11.3	11.4	11.4
930	0.62	0.61	0.60	1150	12.8	12.8	12.8
940	0.71	0.71	0.70	1160	14.2	14.1	14.2
950	0.86	0.84	0.83	1170	16.7	16.2	16.1
960	0.99	0.96	0.95	1180	18.5	18.0	18.0
970	1.14	1.14	1.14	1190	20.6	20.0	20.2
980	1.32	1.32	1.32	1200	23.2	22.2	22.4
990	1.52	1.55	1.55	1210	25.5	24.7	24.9
1000	1.77	1.78	1.78	1220	27.9	27.3	27.5
1010	2.05	2.07	2.06	1230	31.0	30.3	30.3
1020	2.35	2.37	2.35	1240	33.9	33.3	33.3
1030	2.70	2.71	2.70	1250	37.5	36.5	36.5
1040	3.20	3.10	3.05	1260	41.4	39.9	40.0
1050	3.69	3.58	3.54	1270	45.6	43.7	44.0
1060	4.17	4.10	4.04	1280	50.0	47.9	48.2
1070	4.75	4.71	4.69	1290	55.0	52.7	53.0
1080	5.40	5.37	5.35	1300	62.0	57.8	58.2
1090	6.10	6.14	6.16	1310	68.1	63.4	64.2
1100	6.85	6.93	6.98	1320	74.9	69.6	71.0
1110	7.85	7.93	7.94	1330	82.6	75.4	77.9
1120	8.85	8.94	8.94	1340	90.3	83.0	87.0
1130	9.95	10.0	10.0				

Table III is appended to show that the incorrect values given by Nernst's and Henglein's formulæ are equally appreciable when

TABLE III.

$P_{-}$ mm.).	$t$ (Obs. and calc. by vi.) (Ramsay-Young).	$t$ (Calc. by viii.) (Henglein).	$\Delta =$ $t_{\text{Henglein}} - t_{\text{Nernst}}$	$t$ (Calc. by iv.) (Nernst).	$\Delta' =$ $t_{\text{Nernst}} - t_{\text{Henglein}}$
0.76	944°	944°	0	944°	0
1.20	974	974	0	974	0
1.85	1003	1003	0	1003	0
2.81	1032	1033	+1°	1033	+1°
4.18	1060	1061	+1	1061	+1
6.10	1090	1089	-1	1090	0
8.76	1119	1119	0	1119	0
2.4	1148	1149	+1	1150	+2
7.2	1174	1176	+2	1176	+2
13.6	1202	1206	+4	1205	+3
12.0	1234	1238	+4	1237	+3
12.8	1263	1269	+6	1268	+5
16.6	1291	1297	+6	1297	+6
14.1	1319	1327	+8	1325	+6

calculated with reference to temperature, the proportional increase of which is comparatively small.

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CCXCIII.—*Researches on Residual Affinity and Coordination. Part IX. Interaction of Selenium Tetrachloride and  $\beta$ -Diketones.*

By GILBERT T. MORGAN, HARRY DUGALD KEITH DREW, and  
THOMAS VIPOND BARKER.

A COMPARATIVE study of the action of the tetrachlorides of selenium and tellurium on acetylacetone (T., 1920, **117**, 1456) showed that the selenium and tellurium derivatives of this diketone differ in type from the acetylacetone derivatives hitherto obtained from other elements.

This investigation has since been extended to other  $\beta$ -diketones, and the results obtained in condensations with tellurium tetrachloride have recently been described (this vol., p. 922). The present communication deals with selenium derivatives of these ketones.

In the first paper on this subject (*loc. cit.*), it was shown that each of the two tetrachlorides caused the removal of two hydrogen atoms from acetylacetone, giving rise to a bivalent radicle,  $C_5H_6O_2''$ , existing either in tellurium acetylacetone dichloride,  $C_5H_6O_2 \cdot TeCl_2$ , or in the dimeric selenium acetylacetone,  $(C_5H_6O_2)_2Se$ .

A more comprehensive study of these condensations indicates that the organic radicles present in the foregoing compounds are not identical but isomeric. In the tellurium series (this vol., p. 922) the derivatives containing the bivalent radicles in all probability form part of a six-membered cyclic system. But further experiments on the selenium series show that a similar formulation does not explain the observed facts (compare T., 1920, **117**, 1458). The interactions of the two tetrachlorides and the  $\beta$ -diketones are only superficially comparable; more detailed examination has revealed characteristic differences. As bearing on these dissimilarities, the following significant facts should be noted:

(1) Tellurium tetrachloride condenses smoothly with the free  $\beta$ -diketone, whereas the selenium tetrachloride reaction proceeds best with the copper derivative of the diketone.

(2) In the selenium series, condensation is always accompanied by chlorination of a portion of the  $\beta$ -diketone. This reaction is not observed in the tellurium series.

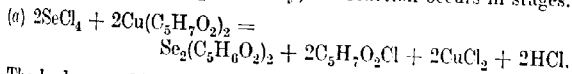
(3) The tellurium derivatives obtained directly from condensation between the tetrachloride and the diketone retain a portion—usually two atomic proportions—of the chlorine. The selenium derivatives are always free from chlorine.

This contrast in the behaviour of the tetrachlorides is probably connected with the differences in the nature and stability of the various chlorides of the two metalloids. Tellurium yields two chlorides,  $\text{TeCl}_2$  and  $\text{TeCl}_4$ , but shows no tendency to form  $\text{Te}_2\text{Cl}_2$ . Selenium, on the contrary, gives most readily  $\text{Se}_2\text{Cl}_2$  and  $\text{SeCl}_4$ . The greater tendency for selenium to accumulate in the molecule is apparent in the majority of the organic derivatives of this metalloid with the  $\beta$ -diketones. In the tellurium series, the derivatives with the diketones contain only one tellurium atom, and when this atom is combined with a bivalent organic radicle the hydrogen atoms removed in forming the unsaturated complex are taken one from a terminal methyl group and one from the enolic group.

The evidence adduced in the experimental part of this communication supports the view that in the condensation of selenium tetrachloride and a  $\beta$ -diketone, or its copper derivative, the hydrogen atoms removed in forming the bivalent group are both taken from the methylene group either directly or indirectly after enolisation and formation of copper derivative. If one of these hydrogen atoms is replaced by ethyl as in *C*-ethylacetylacetone (pp. 2440, 2461), then a bivalent radicle is not produced and selenium attaches itself to univalent radicles. If, on the other hand, the  $\beta$ -diketone contains no terminal methyl group, as is the case with dibenzoylmethane (pp. 2441, 2466), selenium derivatives containing bivalent organic radicles are nevertheless produced.

#### I. *Selenium Tetrachloride and Copper Acetylacetone.*

The predominant chemical change taking place between selenium tetrachloride and copper acetylacetone may be represented in one equation although, in all probability, the reaction occurs in stages.



The hydrogen chloride set free acts destructively on a portion of the dimeric selenium acetylacetone, giving rise to a further proportion of 3-chloroacetylacetone, an adverse reaction which may to some extent be mitigated by using excess of copper acetylacetone; but this addition modifies the principal reaction, so that, together with the main product, selenium acetylacetone, there is also formed a small proportion of *diselenium bisacetylacetone* (VII, see below).

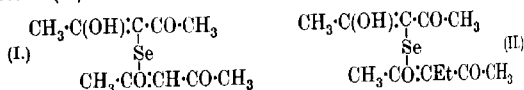
The investigations described below have been undertaken mainly in order to obtain a more conclusive proof of the chemical constitution of selenium acetylacetone. Corroborative evidence has been obtained from a study of the reactions of this selenium compound with acetylacetone and other  $\beta$ -diketones, hydriodic acid, hydrogen cyanide, and the thionaphthols.

*Chemical Constitution of Selenium Acetylacetone.*

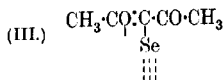
It has already been shown (*loc. cit.*) that selenium acetylacetone is a dimeric compound,  $\text{Se}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ , entirely devoid of enolic properties. The problem of its chemical constitution would be solved by ascertaining from what part of the acetylacetone molecule the two hydrogen atoms are withdrawn in forming the  $\text{C}_5\text{H}_6\text{O}_2^{\cdot}$  radical or rather radicals, for obviously the two groups in the foregoing molecular formula may be isomeric and not identical.

*Selenium OC-bisacetylacetone and Selenium C-ethyl-OC-bisacetylacetone.*—Selenium acetylacetone and acetylacetone combine to form *selenium OC-bisacetylacetone*,  $\text{Se}(\text{C}_5\text{H}_7\text{O}_2)_2$  (I), a monoenolic substance yielding a copper salt, and this additive change can be reversed on heating or by the action of hydroxylic solvents. *C-Ethylacetylacetone* under comparable conditions unites with selenium acetylacetone, forming a similar monoenolic substance, *selenium C-ethyl-OC-bisacetylacetone* (II), and this additive compound is also resolved by heat or hydroxylic solvents into its generators.

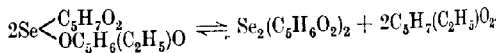
The following formulæ indicate the monoenolic nature of selenium-*OC-bisacetylacetone* (I) and selenium-*C-ethyl-OC-bisacetylacetone* (II).



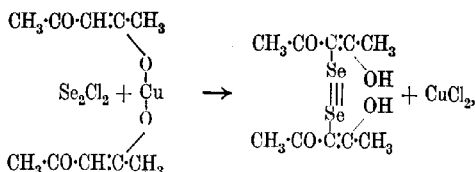
The reversal of the additive change leading to removal of acetylacetone or *C-ethylacetylacetone*, respectively, would leave the residue III, and it is evident from the dimeric condition of selenium



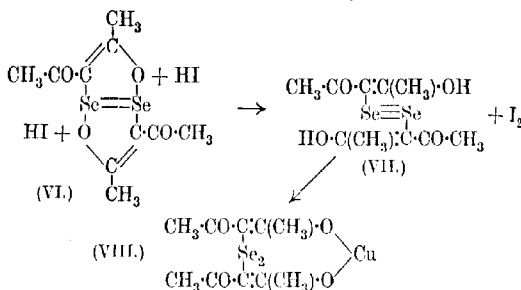
acetylacetone that it is formed by the fusion of two of these unsaturated residues. The following diagram (IV) represents more fully the reversal of the additive change which arises from an interaction of two molecules of selenium *C-ethyl-OC-bisacetylacetone*.







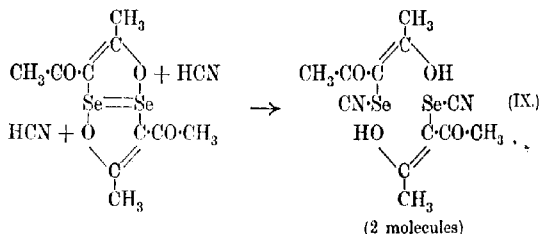
affords confirmatory evidence of the structure assigned to selenium acetylacetonone (VI), inasmuch as the latter substance yields diselenium bisacetylacetonone (VII) on treatment with hydriodic acid.



The foregoing reaction goes quantitatively to completion, and the liberated iodine can be estimated volumetrically.

#### *Selenium Acetylacetonone and Hydrogen Cyanide.*

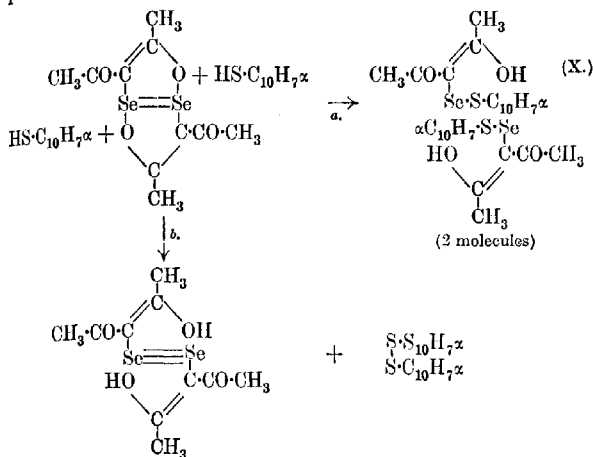
With hydrogen cyanide, the reaction is one of addition and depolymerisation. The product, *cyano-3-selenium acetylacetonone* (IX), exists in the monomeric form, the unsaturated cyanogen groups monopolising the residual affinity of the selenium atoms.



#### *Selenium Acetylacetonone and the Thionaphthols.*

The interactions of selenium acetylacetonone and the aryl thiols occupy an intermediate position between the reactions with hydriodic and hydrocyanic acids. This process has been worked out most

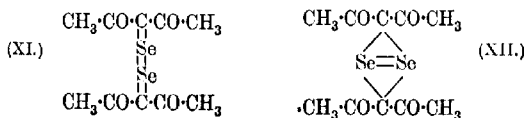
fully with thio- $\alpha$ -naphthol, where the change occurs partly as a simple addition (a) accompanied by depolymerisation, giving  $\alpha$ -naphthylthioselenium acetylacetonc (X), and partly in the direction of forming diselenium bisacetylacetonc and  $\alpha$ - $\alpha$ -dinaphthyl disulphide (b).



The characteristic reactions of selenium acetylacetonc (VII, IX, and X) are capable of wide extension, and already they have been utilised in the synthesis of selenodithionic acid and its salts (T., 1920, **117**, 1461; 1921, **119**, 1066) and in the production of aryl-aminoacetylacetoncs (T., 1921, **119**, 613).

In the foregoing proofs of the constitution of selenium acetylacetonc, the two selenium atoms in dimeric selenium acetylacetonc are represented as forming part of two five-membered cyclic systems, in which each selenium is attached to the median carbon atom of the diketone and to the enolic oxygen, this formulation explaining in a simple and general way the reactions of selenium acetylacetonc with hydriodic and hydrocyanic acids, the aromatic thiols, and the other diketones.

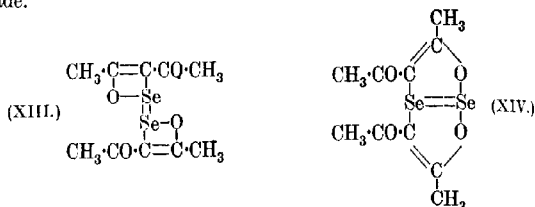
The following formulations (XI and XII) have also been considered and rejected, on the ground that the reaction between selenium





tetrachloride and diketone goes most smoothly with the copper derivative of the latter, in which there is only one mobile hydrogen attached to the central carbon atom. In other words, selenium acetylacetone is to be regarded as derived from the enolic form of the diketone rather than from the diketo-modification. Moreover, the great reactivity of selenium acetylacetone suggests that the selenium is partly united with oxygen so that the cyclic system opens readily at this point of attachment.

There are, however, two other cyclic formulations (XIII and XIV) arising from enolic acetylacetone to which a reference should be made.

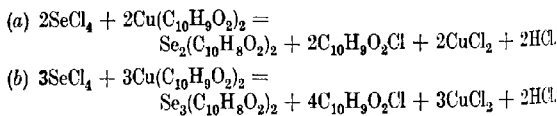


The former of these, containing two four-membered closed chains, might undergo disruption under the influence of hydriodic and hydrocyanic acids, the thiols, the  $\beta$ -diketones, and the bisulphites on account of the comparative instability of four-membered rings.

Formula XIV is the plane symmetric form of the preferred structure (V), which is axially symmetric; it cannot be regarded as representing selenium acetylacetone, because on treatment with hydrocyanic acid or acetylacetone it could not yield, respectively, two molecular proportions of monomeric cyano-3-selenium acetylacetone or of selenium *OC*-bisacetylacetone. The quantitative formation of these additive products indicates that in selenium acetylacetone the two selenium atoms are each situated similarly in the molecule.

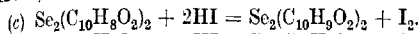
## II. *Selenium Tetrachloride and Copper Benzoylacetone.*

The reaction between selenium tetrachloride and copper benzoylacetone in molecular proportions takes place in two ways:

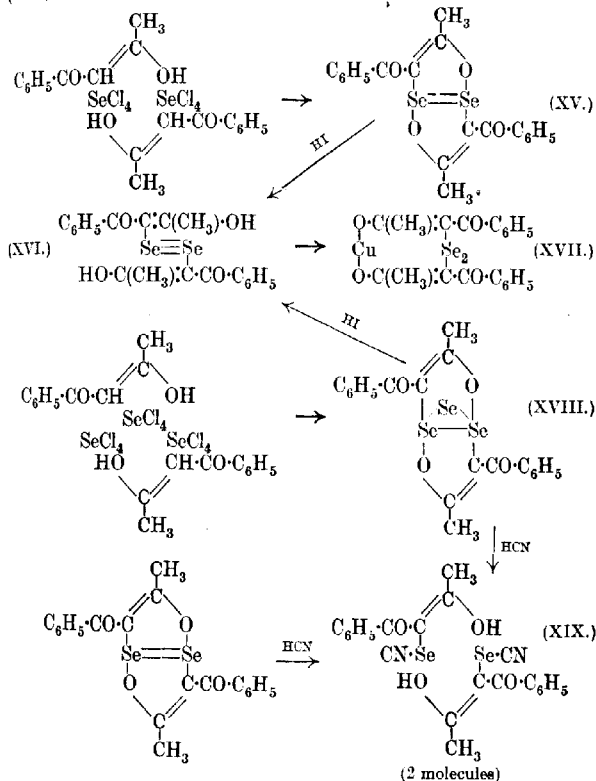


The dimeric form of *selenium benzoylacetone* (XV) is the product

of the simpler condensation (a); the more complex change (b) leads to *cyclotriselenium bisbenzoylacetone* (XVIII). Hydriodic acid converts each of these substances quantitatively into *diselenium bisbenzoylacetone* (XVI) with the liberation of iodine, and in the latter case one-third of the selenium is eliminated. The enolic nature of the product is proved by the formation of its copper salt (XVII).



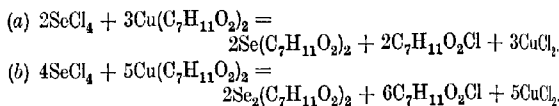
The relationships of these selenium derivatives of benzoylacetone are summarised in the following diagram illustrating their formation and quantitative conversion into diselenium bisbenzoylacetone (XVI), and *cyano-3-selenium benzoylacetone* (XIX):



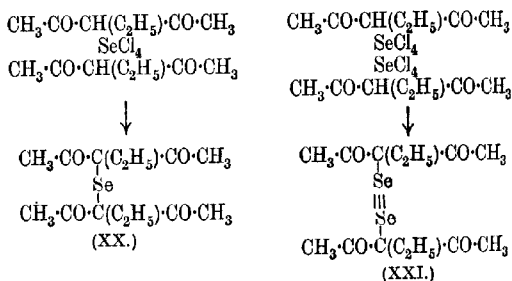
### III. *Selenium Tetrachloride and Copper C-Ethylacetylacetone.*

In the foregoing condensations with the copper salts of acetylacetone and benzoylacetone, non-enolic products containing bivalent radicles,  $C_5H_6O_2''$  and  $C_{10}H_8O_2''$ , respectively, are obtained by the reaction with selenium tetrachloride, thus indicating that the two hydrogen atoms have been removed from the central enolic group,  $-C(OH)=CH-$ .

It became of interest to ascertain what chemical change would occur if an alkyl group was substituted for the hydrogen atom attached to carbon. The case of *C*-ethylacetylacetone was accordingly investigated, the copper derivative of the diketone being employed as in former condensations. Two seleniferous products were obtained, the reaction being represented as follows:



In both these reactions the copper derivative of the diketone furnishes only the univalent radicle,  $C_7H_{11}O_2'$ , thus showing that generally in the replacement of  $\beta$ -diketones the replacement of hydrogen by selenium occurs only at the central methylene complex and not at the terminal methyl groups.



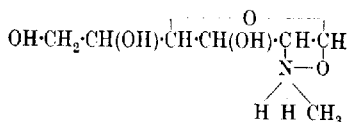
As indicated in the foregoing diagram, when one molecular proportion of selenium tetrachloride is effective the colourless *selenium bis-C-ethylacetylacetone* (XX) is obtained. When two molecular proportions of selenium tetrachloride intervene, yellow *diselenium bis-C-ethylacetylacetone* (XXI) is produced, a compound differing from diselenium bisacetylacetone and diselenium bisbenzoylacetone in being non-enolic, but resembling these orange-coloured derivatives in its degree of complexity.

this condensation, and the reasonable conclusion may be drawn that any substituted glucosamine, in the form of the free base, will react in a similar manner. This expectation has been realised and typical salicylidene derivatives of glucosamine are now described. As these compounds are readily formed, crystallise with ease, and possess convenient solubilities, they are likely to prove of service in developing the chemistry of the amino-sugar.

The method of preparation consists in dissolving the glucosamine salt in water, liberating the free base by the addition of alkali, and then agitating the solution with salicylaldehyde. The salicylidene derivative generally separates directly in the crystalline condition. The properties of five typical examples may now be summarised, as their study has opened out some interesting theoretical considerations.

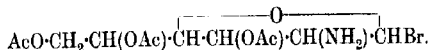
	Colour.	M. p.	$[\alpha]_D$ in methyl alcohol.	Yield per cent.
A. 2-Salicylidene glucosamine	Canary-yellow	183.5°	+ 11.0°	99
B. 2-Salicylidene-1-methyl glucosamine	Deep yellow	120	+ 2.2	26
C. 2-Salicylidene-3 : 5 : 6-tri-acetyl-1-methyl glucosamine	Pale yellow	151	+ 75.7	80
D. 2-Salicylidene-3 : 5 : 6-tri-acetyl-1-ethyl glucosamine	Pale yellow	135	+ 40.7	88
E. 1-Bromo-2-salicylidene-3 : 5 : 6-triacetyl glucosamine	Canary-yellow	118	+ 241.9	65—70

It is significant that with one exception the formation of these salicylidene compounds proceeded with unusual smoothness. The exception is presented by methylglucosamine, which reacted with salicylaldehyde only with difficulty, giving a 26 per cent. yield of the product. This comparative failure to participate in the general reaction cannot be due to the presence of the methyl group in view of the results obtained with the acetylated glucosides, nor can it be attributable to the absence of acetyl groups, as free glucosamine reacted with extreme ease. The abnormal behaviour of methylglucosamine is thus in agreement with the cyclic formula previously suggested for this compound.

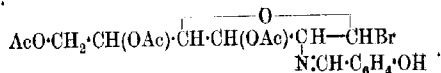


Now, the composition of triacetyl bromoglucosamine, which is the starting point in synthetical work in this series, does not admit of a formula of the above type and the compound must

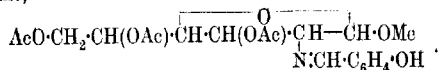
therefore possess the normal structure characteristic of reducing sugars:



It follows that the corresponding salicylidene derivative in which the reactive bromine atom is retained must also be an open chain structure:



When this compound reacts with methyl alcohol to give a "methylglucoside" there seems no reason why profound structural alteration should accompany the change, and the compound formed may be termed 2-salicylidene-3:5:6-triacetyl-1-methyl glucosamine,



The reactions sketched above have been carried out, and the final product proved to be identical with that obtained when salicylaldehyde was condensed with triacetyl methylglucosamine. In other words, no isomerism is involved if the order of introducing the methyl group and the salicylidene residue is varied. The argument leads to the conclusion that triacetyl methylglucosamine is not constituted on the betaine model, but that a change to this type occurs when the acetyl groups are eliminated. It is, of course, possible that triacetyl methylglucosamine may exist in both forms, and in the experimental part a laevorotatory isomeride of this compound is described. This new variety is being further investigated, but the combined results submitted evidently afford strong support to the view formerly expressed that in methylglucosamine the alkyl group is directly attached to the nitrogen atom.

#### EXPERIMENTAL.

##### *Salicylidene Glucosamine.*

Ten grams of glucosamine hydrochloride (1 mol.) and 6.3 grams of sodium bicarbonate ( $1\frac{1}{2}$  mols.) were dissolved in 100 c.c. of water, and 6.3 c.c. of salicylaldehyde (1 mol.) added. The mixture was stirred vigorously at the temperature of the room, and in thirty minutes the separation of crystals commenced. Stirring was continued for three and a half hours, when the product was filtered, washed with cold water, and dried in a vacuum. The yield was 13 grams (99 per. cent.). After recrystallisation from

methyl alcohol, the compound melted sharply at  $183.5^{\circ}$  (Found: C = 54.92; H = 6.18.  $C_{13}H_{17}O_6N$  requires C = 55.09; H = 6.03 per cent.).

Salicylidene glucosamine crystallises in bright yellow needles, insoluble in chloroform, but readily dissolved by hot methyl or ethyl alcohol. The compound was easily hydrolysed by dilute acids, giving salicylaldehyde and the corresponding salt of glucosamine.

*2-Salicylidene-1-methyl Glucosamine* (Salicylidene Methyl-glucosamine).

7.5 Grams of recrystallised methylglucosamine hydrochloride were dissolved in 100 c.c. of water containing 3.75 grams of sodium bicarbonate and 3.2 c.c. of salicylaldehyde. The liquid, which was stirred for two hours, soon acquired a yellow colour and deposited a clear syrup, which adhered to the sides of the vessel. Excess of chloroform was then added and the mixture was shaken repeatedly with this solvent, and after drying the extract over magnesium sulphate, it was evaporated to a small bulk. On the addition of light petroleum, the product separated in a semi-crystalline condition. Purification was effected by again dissolving in chloroform and precipitating in the manner described above, salicylidene methylglucosamine being thus obtained in bright yellow needles melting at  $120^{\circ}$ . The yield from the experiment just described was 1.7 grams (26 per cent.), and this was not improved in subsequent preparations [Found: C = 56.33; H = 6.41; OMe = 9.63.  $C_{13}H_{16}O_5N(OMe)$  requires C = 56.56; H = 6.39; OMe = 10.47 per cent.]. Salicylidene methylglucosamine is readily hydrolysed by acids to regenerate methylglucosamine. On the other hand, the action of nitrous acid involves the removal of the salicylidene residue followed by the elimination of the amino- and glucosidic groups.

*2-Salicylidene-3:5:6-triacetyl-1-methyl Glucosamine* (Salicylidene Triacetyl Methylglucosamine).

Two distinct methods were employed in the preparation of this compound and their significance is referred to in the introduction.

*Method I.*—A solution of 5.3 grams of 1-bromo-2-salicylidene-3:5:6-triacetyl glucosamine in 30 c.c. of methyl alcohol was mixed with 3.2 grams of morphine, dissolved in 60 c.c. of the same solvent. When the mixture was kept at the temperature of the room for seven days, morphine hydrobromide gradually separated. The filtrate, on evaporation under diminished pressure, gave a solid residue, which was recrystallised from alcohol. Yield 50 per cent.

*Method II.*—8.2 Grams of recrystallised triacetyl bromoglucosamine hydrobromide were dissolved in 100 c.c. of methyl alcohol containing 1.65 c.c. of pyridine. The solution was set aside for twenty hours, filtered, and concentrated to a small bulk at 25°/90 mm. Thereafter a solution of 3.5 grams of sodium bicarbonate in 40 c.c. of water was added together with 1.95 c.c. of salicylaldehyde. Vigorous stirring occasioned the separation of the crystalline product, which, after thirty minutes, was filtered and washed with cold water. One recrystallisation from alcohol gave a pure product melting at 151—152°. Yield 80 per cent. (Found: C = 56.93; H = 6.25; OMe = 8.2.  $C_{20}H_{25}O_9N$  requires C = 56.71; H = 5.95; OMe = 7.3 per cent.). The salicylidene derivative crystallises in pale yellow, prismatic needles readily soluble in hot alcohol;  $[\alpha]_D$  in methyl alcohol + 75.7° for  $c = 1$ . The three acetyl groups in the compound are remarkably stable, but were quantitatively removed by distillation with 15 per cent. sulphuric acid. After four hours' treatment with absolute alcohol saturated with ammonia at 0°, no acetamide was formed, and 70 per cent. of the original material was recovered unaltered (Fischer, *Ber.*, 1914, 47, 218).

*Action of Nitrous Acid.*—When salicylidene triacetyl methylglucosamine was suspended in water and an aqueous solution of nitrous acid (prepared from silver nitrite) gradually added with vigorous stirring, no visible reaction ensued until the temperature was raised to 50°. The solid then passed into solution with copious evolution of nitrogen and liberation of salicylaldehyde. On neutralising the solution with barium carbonate, a quantity of salicylidene triacetyl methylglucosamine was regenerated and was precipitated in the crystalline state. The filtrate was evaporated to dryness under diminished pressure and extracted with boiling alcohol. This extract contained a glucosidic syrup, which was deacetylated by boiling with acidified methyl alcohol. After neutralisation with silver carbonate and removal of the solvent, a non-crystalline syrup remained which behaved as a glucoside towards Fehling's solution, but could not be identified either as methylglucoside or methylmannoside.

2-Salicylidene-3 : 5 : 6-triacetyl-1-ethyl Glucosamine (Salicylidene Triacetyl Ethylglucosamine).

Starting from triacetyl ethylglucosamine, the usual method of preparation was employed and gave an 88 per cent. yield of the above product [Found: C = 57.51; H = 6.39; OEt = 10.14.  $C_{20}H_{24}O_8N(OEt)$  requires C = 57.63; H = 6.18; OEt = 10.29 per cent.]. In every respect the compound resembled the corre-

sponding methyl derivative, m. p.  $131^{\circ}$ ,  $[\alpha]_D$  in methyl alcohol  $+40.7^{\circ}$  for  $c = 1$ .

3:5:6-Triacetyl-1-methyl Glucosamine (Triacetyl Methylglucosamine).

For reasons given in the introduction, the preparation of this compound from triacetyl bromoglucosamine was repeated.

(a) *Using pyridine*: The method adopted was identical with that described by Irvine, McNicoll, and Hynd (*loc. cit.*), and the properties previously assigned to the product were confirmed. The specific rotation in methyl alcohol was, however, slightly higher ( $+23.3^{\circ}$  in place of  $+20^{\circ}$ ).

(b) *Using morphine*: This preparation was conducted according to the variation recommended by Irvine and Hynd (T., 1912, **101**, 1137) and the crude product was crystallised repeatedly by solution in methyl alcohol and the addition of ether. The finely divided solid was then extracted with methyl alcohol in the cold, the filtrate being concentrated and precipitated with ether. Repetition of these processes gave a small, crystalline crop which decomposed at  $201-202^{\circ}$  and showed  $[\alpha]_D$  in methyl alcohol  $-14.6^{\circ}$  for  $c = 1.8656$  [Found: C = 39.00; H = 5.79; OMe = 8.0.  $C_{12}H_{18}O_7 \cdot N(OMe) \cdot HBr$  requires C = 38.99; H = 5.55; OMe = 7.75 per cent.]. No morphine aminoglucoside was present, and the compound is thus a new stereoisomeric form of triacetyl methylglucosamine hydrobromide.

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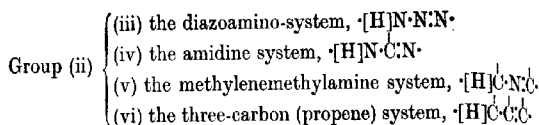
CCCLXXXVII.—*The Mobility of Symmetrical Triad Systems. Part I. The Conditions Relating to Systems Terminated by Phenyl Groups.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT.

It is the purpose of this series of papers to examine comparatively the mobility of symmetrical tautomeric systems of the general formula  $[H]X \cdot Y \cdot X$ . Six systems fall within the purview of this subject:

- Group (i)  $\begin{cases} \text{(i) the carboxyl group, } [H]O \cdot \overset{\overset{O}{\parallel}}{C} \cdot O \\ \text{(ii) the acinitro-group, } [H]O \cdot \overset{\overset{O}{\parallel}}{N} \cdot O \end{cases}$





With regard to the first two (group i), the circumstantial evidence as to the equivalent functions of the two oxygen atoms is of the strongest character, but only the last four systems (group ii) are capable of being investigated as regards their mobility by the methods illustrated in this paper. It is proposed to investigate the behaviour of these four systems when attached to different types of terminal group, the present paper being primarily concerned with the terminal phenyl group, and hence with the comparison of the following four substances :



Some of the data necessary for this comparison are already on record and the remainder is given in the experimental portion of this paper.

The proof of the mobility of the three-nitrogen system present in diazoaminobenzene (I) rests on two types of evidence, both of which find their parallel in the experiments described hereunder :

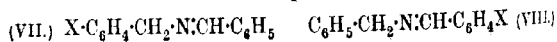
(A) Proof that only a single substitution product exists where two substances having formulae (V) and (VI) might be expected (Griess, *Annalen*, 1866, **137**, 60; *Ber.*, 1874, **7**, 1619; and others).

(B) Proof that the single individual referred to under (A), on fission at the double bond (as by reduction or hydrolysis), gives four products, two derived from the two fragments of each of the hypothetical substances (V) and (VI) (Noelting and Binder, *Ber.*, 1887, **20**, 3005; and others).



The same two types of evidence have been advanced in relation to diphenylformamidine (II) and its derivatives (Marckwald, *Annalen*, 1895, **286**, 348; von Pechmann, *Ber.*, 1897, **30**, 1783, and earlier; Wheeler and Johnson, *Ber.*, 1899, **32**, 35, and earlier).

In view of these facts, it was at first a matter for surprise to us on turning to the third of the four systems under comparison that both the above mobility tests (A and B) failed when applied to derivatives of benzylidenemethylamine (III). Pairs of isomeric monosubstitution products of the general types (VII) and (VIII), as well as similar disubstitution products, not only were different

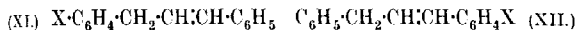


from one another, but also, apparently, were quite incapable of interconversion. Each individual, moreover, on fission, by acid hydrolysis, at the double bond gave two and not four resultants, the two being the aldehyde and amine by the interaction of which the substance in question was originally prepared (examples, pp. 2385, 2386).

The three-carbon system present in  $\alpha\gamma$ -diphenylpropene (IV) has a special interest in view of the close analogy between this substance and glutaconic acid, the three-carbon system of which is known to possess a high degree of mobility. The application to glutaconic acid of method (A) (above) was accomplished by Thole and Thorpe (T., 1911, 99, 2193), who proved that  $\alpha$ - and  $\gamma$ -alkyl derivatives, which, from the manner of their synthesis, would be expected to have formulæ such as (IX) and (X), were actually identical; on



the other hand, evidence of type (B) is to be found in the recent experiments of Feist, who, in several instances, obtained four products on fission by oxidation with ozone, two corresponding with each of the two static formulæ of the substance (*Annalen*, 1922, 428, 51, 71). The glutaconic acids, therefore, respond to both mobility tests, and it was fully expected that the  $\alpha\gamma$ -diphenylpropenes, in view of their close relationship with the glutaconic acids, would behave in an analogous manner. It was found, however, that the two phenyl groups in diphenylpropene are not equivalent, and that corresponding substitution products of types (XI) and (XII) show no tendency to undergo conversion one into the other (test A); each individual, moreover, on oxidation by



permanganate (test B) gives, not four, but two fission products corresponding with the particular static formula assigned to the substance (examples, pp. 2386, 2389).

From the above summary it will be evident that the molecular machinery necessary to produce a condition of tautomerism cannot consist solely of the formal "tautomeric system" and a potentially mobile hydrogen atom in the correct position. Some activating factor or condition must also be present, for only on this supposition can we account for the contrasts to which attention has been directed. As to the nature of this factor, a certain amount of guidance can be obtained from a consideration of tautomerism in relation to certain other properties of the systems under review. It seems reasonable, *a priori*, to assume as a condition of first importance in the determination of mobility that the  $\alpha$ -hydrogen atom should be capable of being easily detached from the tautomeric

system. In the carboxyl and acinitro-groups (systems i and ii), the mobility of which is probably much greater than in any other case, we have clear evidence of the easy detachment of the mobile hydrogen atom in the facility with which it can be replaced by an alkyl group (esterification). The mobile hydrogen atom in diazo-aminobenzene can also be replaced by an alkyl group, but it is necessary in this case to use alcoholic sodium ethoxide and an alkyl iodide, just as in the alkylation of unsymmetrical systems such as that present in ethyl acetoacetate. The same is true of amidines and glutaconic esters. It will be observed that in all these cases the systems capable of alkylation are mobile systems. On the other hand,  $\alpha,\gamma$ -diphenylpropene (although formally so similar to glutaconic acid) and benzyldenebenzylamine cannot be alkylated by the ordinary methods; both these types are non-tautomeric. Evidently, the concurrence is far-reaching, but to what extent it will hold in border-line cases such as that of indene, which is alkylated with difficulty, it remains for future experiments to show. Indene, and the analogues of indene and of glutaconic acid containing the system  $\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}\cdot$  in place of  $\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot$ , are cases the examination of which is in progress.

From the above parallelism it is possible to draw two conclusions relating to the conditions necessary for the activation of a potentially tautomeric system: (a) that the activating condition is dependent primarily on the  $\alpha$ -atom of the system, and is associated with the easy detachment of hydrogen from this position; (b) that the activating condition is one of the well-recognised group of related characteristics generally supposed to be associated with negative electrical polarity. Hence it is that the greatest mobility is observed when the  $\alpha$ -atom is oxygen (systems i and ii), intermediate mobility when it is nitrogen (systems iii and iv), and least mobility when it is carbon (systems v and vi); hence, also, the fact that in the last case mobility is only observed when a definite negative polarity is "induced" by strongly polar attached groups, as in the glutaconic acids. It must be admitted that questions of polarity are but little understood at present, and that much more information is required before the somewhat approximate generalisations given above can be replaced by a precise statement of the conditions for tautomerism, the complete elucidation of which forms the object of researches now in progress.

#### EXPERIMENTAL.

##### (A)—Preparation of *m*- and *p*-Nitrobenzylamine.

These bases were prepared by Gabriel's method. Hafner (*Ber.*, 1890, 23, 338) has prepared *p*-nitrobenzylamine in this way, but

gives no details. In preparing large quantities, it was found convenient to hydrolyse the phthalimides by sulphuric acid, in place of hydrochloric acid at  $200^{\circ}$ , the reagent employed by Gabriel.

The phthalimides were prepared by heating the appropriate nitrobenzyl chlorides with potassium phthalimide for half an hour by means of an oil-bath, the temperature of which was gradually raised during this period from  $100^{\circ}$  to  $115^{\circ}$ . It is essential to adhere to these conditions, as otherwise, either condensation may not take place, or the whole mass may suddenly carbonise with large evolution of gas. In any case, it is advisable to keep the mixture under close observation and add water at the first signs of self-heating. The product was isolated in the manner described by Gabriel (*Ber.*, 1887, **20**, 2227) for the ortho-compound.

The crude washed phthalimide, dissolved in the minimal quantity of cold concentrated sulphuric acid, was treated with water until the precipitate first formed just failed to redissolve. The solution was heated until a test portion gave no precipitate on cooling and diluting with water, then diluted, rendered strongly alkaline with sodium hydroxide, and extracted with ether. The base was extracted from the ether by dilute hydrochloric acid, from which it was recovered in the form of its hydrochloride by evaporation.

(B)—*Preparation of Isomeric m-Nitro-, p-Nitro-, and mp-Dinitro-derivatives of Benzylidenbenzylamine.*

*General Method of Preparation.*—Equivalent quantities of the appropriate aldehyde and amine were mixed in ethereal solution at the ordinary temperature. The ether was allowed to evaporate and the product crystallised.

*General Properties.*—The following six substances are stable towards water and dilute alkalis, but are hydrolysed by mineral acids into the aldehyde and amine from which they were formed.

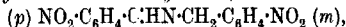
*Benzylidene-p-nitrobenzylamine*,  $C_6H_5 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol in dense prisms, m. p.  $71^{\circ}$  (Found: C = 70.0; H = 5.4.  $C_{14}H_{12}O_2N_2$  requires C = 70.0; H = 5.0 per cent.).

*p-Nitrobenzylidenbenzylamine*,  $C_6H_5 \cdot CH_2 \cdot N:CH \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol or ligroin in laminae, m. p.  $56^{\circ}$  (Found: C = 70.3; H = 5.4 per cent.).

*Benzylidene-m-nitrobenzylamine*,  $C_6H_5 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , separates from alcohol in short, dense prisms, m. p.  $42^{\circ}$  (Found: C = 69.8; H = 5.2 per cent.).

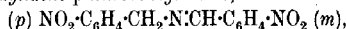
*m-Nitrobenzylidenbenzylamine*,  $C_6H_5 \cdot CH_2 \cdot N:CH \cdot C_6H_4 \cdot NO_2$ , separates from alcohol in long, thin laminae, m. p.  $62^{\circ}$  (Found: C = 70.1; H = 5.3 per cent.).

*p*-Nitrobenzylidene-*m*-nitrobenzylamine,



crystallises from ethyl acetate in colourless needles, *m. p.* 115° (Found: N = 14.7.  $\text{C}_{14}\text{H}_{11}\text{O}_4\text{N}_3$  requires N = 14.7 per cent.). This *m. p.* is the same as that of the next compound, but a mixture of the two melted below 100°.

*m*-Nitrobenzylidene-*p*-nitrobenzylamine,

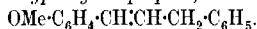


crystallises from ethyl acetate in needles, *m. p.* 115° (Found: N = 14.8 per cent.).

(C)—Condensation of  $\beta$ -Phenylpropionic Acid with Anisaldehyde; Formation of *p*-Methoxy- $\alpha$ -benzylcinnamic Acid and  $\alpha$ -Phenyl- $\gamma$ -*p*-methoxyphenyl- $\Delta^2$ -propene.

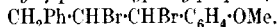
Sodium  $\beta$ -phenylpropionate (150 grams = 1 mol.), anisaldehyde (105 grams = 1 mol.), and acetic anhydride (105 grams = 1.2 mols.) were heated together for nine hours at 152°. The product was poured into an excess of sodium carbonate solution, distilled in a current of steam to remove the excess of anisaldehyde, and extracted with ether.

$\alpha$ -Phenyl- $\gamma$ -*p*-methoxyphenyl- $\Delta^2$ -propene,



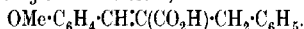
—The viscous, yellow oil which remained when the ether was dried and evaporated consisted largely of the methoxy-hydrocarbon, but it also contained a little anisaldehyde and some material which decomposed on distillation. After two distillations the methoxy-hydrocarbon was obtained as a colourless oil which boiled constantly at 227°/30 mm. (Found: C = 85.4; H = 7.3.  $\text{C}_{16}\text{H}_{16}\text{O}$  requires C = 85.7; H = 7.2 per cent.). The substance was characterised by means of its dibromo-additive product.

$\beta\gamma$ -Dibromo- $\alpha$ -phenyl- $\gamma$ -*p*-methoxyphenylpropane,



—Two grams of the methoxy-hydrocarbon, dissolved in 2 c.c. of chloroform and cooled to 0°, decolorised 5.8 c.c. of a solution of bromine in chloroform containing 0.253 gram per c.c. (theoretical for 2Br = 5.67 c.c.). No perceptible amount of hydrogen bromide was evolved. The bromo-compound, which crystallised from the chloroform (a second crop was obtained after concentration), melted at 115°, and recrystallisation from light petroleum did not alter this melting point (Found: Br = 41.8.  $\text{C}_{16}\text{H}_{16}\text{OBr}_2$  requires Br = 41.6 per cent.). The compound forms stout prisms terminated by pyramids; it is easily soluble in the usual organic solvents.

*p*-Methoxy- $\alpha$ -benzylcinnamic Acid,



—The alkaline solution from which the methoxy-hydrocarbon was

extracted was heated to the boiling point, treated with excess of hydrochloric acid, and the precipitated acids collected while hot. Most of the  $\beta$ -phenylpropionic acid passed through the filter as an oil, and the remainder was removed after cooling by washing with a little cold alcohol. The residue, which consisted of a mixture of *p*-methoxycinnamic acid and *p*-methoxy- $\alpha$ -benzylcinnamic acid, was heated on the steam-bath for ten minutes with 100 c.c. of 2*N*-aqueous sodium carbonate. *p*-Methoxy- $\alpha$ -benzylcinnamic acid is only slowly soluble in dilute sodium carbonate, which, under the conditions described, dissolved all the *p*-methoxycinnamic acid but only part of the *p*-methoxy- $\alpha$ -benzylcinnamic acid; the undissolved portion was collected and recrystallised from ethyl alcohol (12 grams). The acids dissolved by the sodium carbonate were fractionally precipitated by the addition of successive portions of 10 c.c. of 2*N*-hydrochloric acid. The first two precipitations yielded *p*-methoxy- $\alpha$ -benzylcinnamic acid sufficiently free from *p*-methoxycinnamic acid to be capable of complete purification by crystallisation from alcohol (9.7 grams). The third and fourth precipitations gave mixtures which, when combined and subjected to a second series of fractional precipitations, gave 2.0 grams of *p*-methoxy- $\alpha$ -benzylcinnamic acid. The residual alkaline solutions were treated with excess of hydrochloric acid, and the recovered *p*-methoxycinnamic acid was crystallised from alcohol. In all, 23.7 grams of pure *p*-methoxy- $\alpha$ -benzylcinnamic acid were obtained along with 14.5 grams of pure *p*-methoxycinnamic acid.

*p*-Methoxy- $\alpha$ -benzylcinnamic acid crystallises from alcohol in colourless, flattened needles, m. p. 170°. It is readily soluble in aqueous sodium hydroxide, but dissolves only slowly in hot sodium carbonate solution and is evidently an unusually weak acid. It instantly decolorises cold alkaline permanganate, giving anisic acid, phenylacetic acid, and benzoic acid (Found: C = 75.9; H = 6.1.  $C_{17}H_{16}O_3$  requires C = 76.1; H = 6.1 per cent.).

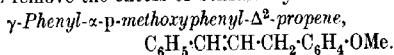
The *anilide* was obtained by adding a small excess of aniline to the chloride of *p*-methoxy- $\alpha$ -benzylcinnamic acid, which was prepared by digesting the acid with thionyl chloride. It crystallised from alcohol in long, silky needles, m. p. 159° (Found: C = 80.2; H = 6.4.  $C_{23}H_{21}O_2N$  requires C = 80.4; H = 6.1 per cent.).

(D)—*Condensation of p-Methoxy- $\beta$ -phenylpropionic Acid with Benzaldehyde; Formation of  $\alpha$ -p-Methoxybenzylcinnamic Acid and  $\gamma$ -Phenyl- $\alpha$ -p-methoxyphenyl- $\Delta^2$ -propene.*

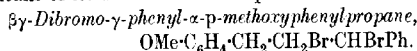
*p*-Methoxy- $\beta$ -phenylpropionic acid was prepared by Perkin's method from anisaldehyde (T., 1877, **31**, 408, 411).

Sodium *p*-methoxy- $\beta$ -phenylpropionate (110 grams), benzaldehyde

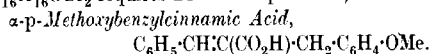
(70 grams); and acetic anhydride (70 grams) were heated together for nine and a half hours at 150°, and then poured into an excess of aqueous sodium carbonate and distilled in a current of steam to remove the excess of benzaldehyde.



—This was isolated by extracting the alkaline liquid with ether, and purified by fractional distillation. The more volatile fractions contained benzaldehyde, but after two distillations the methoxy-hydrocarbon was obtained as a colourless, and nearly odourless oil, b. p. 220°/25 mm. (Found: C = 84.7; H = 7.2.  $\text{C}_{16}\text{H}_{18}\text{O}$  requires C = 85.7; H = 7.2 per cent.). It was characterised by means of its dibromo-additive product.



—This substance was prepared by the action of two atoms of bromine on the above methoxy-hydrocarbon in chloroform solution at 0°, the experiment being conducted just as in the case of the isomeric bromo-compound (p. 2386). The new compound separated from ligroin in colourless prisms, m. p. 76° (Found: Br = 41.8.  $\text{C}_{16}\text{H}_{16}\text{OBr}_2$  requires Br = 41.6 per cent.).



—The alkaline liquid from which the above methoxy-hydrocarbon had been extracted was heated to boiling and acidified with hydrochloric acid, which precipitated an oil consisting of a mixture of cinnamic acid, *p*-methoxy-β-phenylpropionic acid, and *α-p*-methoxybenzylcinnamic acid. The last is much less soluble in boiling water than either of the others. The oil was separated from the aqueous layer, boiled with two litres of water, and the undissolved portion, which had solidified, was collected and crystallised twice from alcohol, from which 16 grams of pure *α-p*-methoxybenzylcinnamic acid separated in colourless, glistening needles, m. p. 165° (Found: C = 76.3; H = 6.4.  $\text{C}_{17}\text{H}_{16}\text{O}_3$  requires C = 76.1; H = 6.1 per cent.). The aqueous liquids deposited a mixture of cinnamic acid and *p*-methoxy-β-phenylpropionic acid on cooling.

*α-p*-Methoxybenzylcinnamic acid instantly decolorises cold alkaline permanganate, forming *p*-methoxyphenylacetic acid, aniseic acid, and benzoic acid. Like its isomeride (p. 2386), it is a very weak acid: it is insoluble in cold sodium carbonate solution, although it dissolves slowly on boiling; it is easily soluble in sodium hydroxide.

The *anilide*, obtained by adding a small excess of aniline to the acid chloride, which was prepared by digesting the acid with thionyl

chloride, crystallised from alcohol in short, thick prisms or, occasionally, in needles, m. p. 140—141° (Found: C = 80.4; H = 6.6.  $C_{22}H_{21}O_2N$  requires C = 80.4; H = 6.1 per cent.).

We desire to thank the Royal Society for defraying a large part of the cost of this work.

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[Received, July 14th, 1922.]

## CCLXXXVIII.—Dyes Derived from "Saccharin." The Sulphamphthaleins.

By SIKHIBHUSHAN DUTT.

A NUMBER of sulphonephthaleins have already been prepared by the aid of *o*-sulphobenzoic acid (Remsen, *J. Amer. Chem. Soc.*, 1885, 7, 180; compare also *ibid.*, 1887, 9, 372; Blackshear, *ibid.*, 1892, 14, 455; Remsen and MacKee, *ibid.*, 1896, 18, 794; Lubs and Clark, *J. Washington Acad. Sci.*, 1915, 5, 609).

The difficulty of getting pure *o*-sulphobenzoic acid in good yield led the author to investigate the action of "saccharin" on amines and phenols. In this way, condensation products have been obtained which are characterised by their colour and fluorescence and closely resemble the corresponding phthaleins in constitution and behaviour. They differ from the corresponding sulphonephthaleins in having the bivalent imido-group in place of the lactone oxygen atom. Accordingly, they have been named *sulphamphthaleins*.

The trimethyl derivative of phenolsulphamphthalein is obtained by the action of methyl sulphate on the trisodium salt, but only the diacetyl and the dibenzoyl derivatives are obtained by similar treatment with acetyl chloride and benzoyl chloride, respectively. The diacetyl derivative is more conveniently obtained by the action of acetic anhydride and pyridine on phenolsulphamphthalein itself.

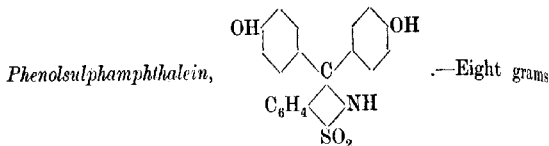
The following amino- and hydroxy-compounds have been condensed with "saccharin": phenol, resorcinol, orcinol, phloroglucinol, hydroxyquinol, catechol, 1:2:4:5-tetrahydroxybenzene, *m*-phenylenediamine, *m*-aminophenol, *m*-dimethylaminophenol, and 4:6-diaminoresorcinol. The colour and dyeing properties of the products closely resemble those of the corresponding phthaleins, but the fluorescence is somewhat stronger. They all decompose on heating.

The "saccharin" employed in the above-mentioned condensations was obtained by extracting the commercial material with sodium hydrogen carbonate, treating the solution with hydro-



chloric acid, and fractionally crystallising the precipitate from ether, the portion melting at 218–220° being utilised.

## EXPERIMENTAL.



of "saccharin," 15 grams of phenol, and 5 c.c. of concentrated sulphuric acid were heated together at 100–110° for ten hours. The excess of phenol was distilled off in steam, and the brownish-red residue purified by dissolving it in ammonia and treating the filtered solution with dilute hydrochloric acid. The precipitate crystallised from hot water in yellow prisms, which became red on rubbing. The yield was 15 per cent. of the theoretical. With zinc chloride at 160° as the condensing agent, the yield is only 6 per cent.

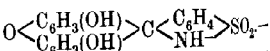
Like phenolphthalein, phenolsulphamphthalein dissolves in alkali with a pink colour. It dissolves in water, acetic acid, or alcohol with a yellow colour, but is insoluble in ether. It has been obtained in two chromoisomeric forms, yellow and red, the former being the more unstable (Found : S = 9.1; N = 4.1.  $C_{19}H_{15}O_4NS$  requires S = 9.1; N = 3.9 per cent.).

The *trisodium* salt, prepared by neutralising an aqueous solution of the sulphamphthalein with N/2-sodium hydroxide (3 equivalents were required) and evaporating the solution to dryness, is a dark red, crystalline substance, which dissolves in water with a brilliant pink colour and is extremely hygroscopic.

The *trimethyl* derivative was prepared by the action of methyl sulphate on the trisodium salt. It crystallises from dilute acetic acid in colourless needles melting at 142° (Found : C = 67.5; H = 5.6.  $C_{22}H_{21}O_4NS$  requires C = 67.8; H = 5.3 per cent.).

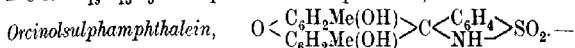
A *dibenzoyl* derivative was prepared by the action of benzoyl chloride on the sodium salt. It crystallises from hot water in colourless, silky needles melting at 127° (Found : C = 70.5; H = 4.2.  $C_{33}H_{24}O_6NS$  requires C = 70.7; H = 4.3 per cent.).

The *diacetyl* derivative, prepared by means of acetic anhydride and pyridine, crystallises from dilute alcohol in colourless needles, m. p. 112° (Found : C = 62.8; H = 4.4.  $C_{23}H_{19}O_6NS$  requires C = 63.15; H = 4.3 per cent.).

Resorcinolsulphamphthalein,  .—Eight grams of "saccharin," 11 grams of resorcinol, and 10 grams of

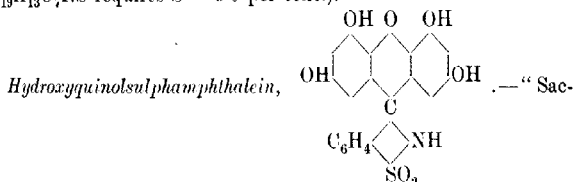
fused zinc chloride were heated at 180—190° for two hours, when the melt became almost solid. The cooled product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, washed with water, and extracted with ether to remove unchanged "saccharin." The product was converted, by the action of lead acetate on the sodium salt, into the lead lake, which was dried, suspended in absolute alcohol, and decomposed by hydrogen sulphide. The alcoholic solution was filtered, concentrated to a small volume, and the dye precipitated with ether, being obtained in microscopic, brownish-yellow needles.

*Resorcinolsulphamphthalein* is very soluble in alcohol or acetic acid, moderately soluble in water, and insoluble in ether or light petroleum. It dissolves in alkali with an orange colour, and the solution on dilution shows a very intense yellowish-green fluorescence. The sodium salt dyes light yellow shades on wool (Found:  $S = 8.4$ .  $C_{19}H_{13}O_5NS$  requires  $S = 8.7$  per cent.).



Eight grams of "saccharin," 13 grams of orcinol, and 11 grams of fused zinc chloride were heated at 180° for about three hours, and the product was isolated as described above. It crystallises from dilute alcohol in brownish-yellow needles and dissolves in alkali with a blood-red colour, the solution, on dilution, showing a brilliant green fluorescence. The sodium salt dyes pink shades on wool (Found:  $S = 7.9$ .  $C_{21}H_{17}O_5NS$  requires  $S = 8.1$  per cent.).

*Phloroglucinsulphamphthalein*.—Prepared from 3.6 grams of "saccharin," 5 grams of phloroglucinol, and 4 grams of fused zinc chloride at 180—190° in about twenty minutes, and isolated in the manner already described, this compound crystallised from hot water in long, brownish-yellow needles. It dissolves in alkali with an orange-red colour, but the solution is not fluorescent. The sodium salt dyes fine orange shades on wool (Found:  $S = 8.3$ .  $C_{19}H_{13}O_7NS$  requires  $S = 8.0$  per cent.).



charin" (1.8 grams), hydroxyquinol (2.5 grams), and fused zinc chloride (2 grams) were heated at 160—170° for two hours while a slow stream of dry hydrogen was passed over the molten mass. Purification by means of sodium hydroxide solution having been

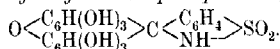
found ineffective, the product was acetylated. The *acetyl* derivative crystallised from dilute alcohol in colourless prisms melting above 300°. The product of its hydrolysis by alkali crystallises from a mixture of alcohol and ether in light reddish-brown, silky needles.

*Hydroxyquinolsulphamphthalein* is very soluble in alcohol or acetic acid, moderately soluble in hot water, and sparingly soluble in ether or cold water. It dissolves in alkali with a pink colour, the solution showing a feeble yellow fluorescence. The sodium salt dyes fine pink shades on wool (Found : S = 7.8.  $C_{18}H_{13}O_7NS$  requires S = 8.0 per cent.).

*Catecholsulphamphthalein*.—Eight grams of "saccharin," 11 grams of catechol, and 10 grams of fused zinc chloride were heated at 180–190° for three hours. The cold product was powdered, washed with concentrated hydrochloric acid, and crystallised from ether, minute brown needles being obtained.

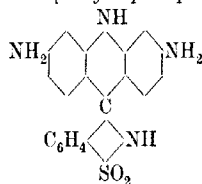
*Catecholsulphamphthalein* is very soluble in water, alcohol, or acetic acid, and sparingly soluble in ether. It dissolves in alkalis with a green colour (Found : S = 8.6.  $C_{19}H_{13}O_5NS$  requires S = 8.7 per cent.).

1 : 2 : 4 : 5-Tetrahydroxybenzenesulphamphthalein,



—"Saccharin" (0.8 gram) and 1 : 2 : 4 : 5-tetrahydroxybenzene (1.4 grams) were heated at 160° with 0.5 gram of fused zinc chloride for about two hours. The product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, dried, and acetylated by the usual method. The *hexa-acetyl* derivative crystallised from dilute acetic acid in white, silky needles which did not melt at 290° (Found : C = 54.1; H = 3.6.  $C_{31}H_{25}O_{15}NS$  requires C = 54.5; H = 3.7 per cent.). On hydrolysis with alkali, the pure dyestuff was obtained, which crystallised from hot water in dark brown needles with a green, metallic lustre. It dissolves in alkali with a pink colour but without fluorescence (Found : S = 7.0.  $C_{19}H_{13}O_6NS$  requires S = 7.4 per cent.).

4 : 4'-Diamino-2 : 2'-iminophenylsulphamphthalein,

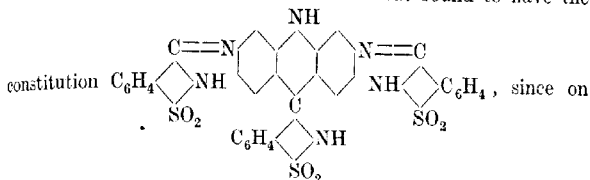


—"Saccharin" (1.8 grams) and *m*-phenylenediamine hydrochloride

(3.6 grams) were heated at  $230^{\circ}$  for about fifteen minutes. The melt was extracted with ether to remove unchanged "saccharin" and dissolved in hot alcohol. The alcoholic solution, on cooling, deposited a quantity of brown needles, which were removed. The mother-liquor was concentrated to small bulk and cautiously diluted with water, when the sulphamphthalein was deposited in bright yellow, prismatic needles (Found: S = 8.7; N = 15.1.  $C_{19}H_{16}O_2N_4S$  requires S = 8.7; N = 15.4 per cent.).

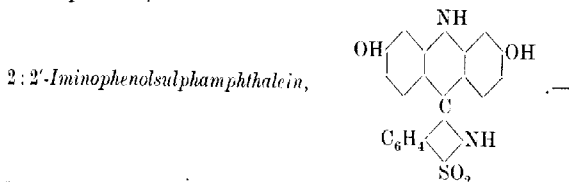
The substance is very soluble in alcohol or acetic acid, sparingly soluble in water, and insoluble in ether. Its solution shows an intense yellow-green fluorescence, which is very similar to that of fluorescein.

The above-mentioned brown substance was found to have the



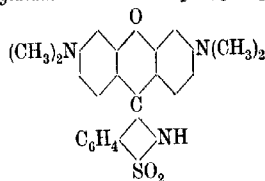
boiling with alkali it decomposed yielding "saccharin" and the diaminoiminophenylsulphamphthalein. It was also formed when these two substances were heated with zinc chloride at  $160^{\circ}$ .

It is slightly soluble in alcohol or acetic acid, and insoluble in water or ether. The solution shows a brilliant green fluorescence (Found: S = 13.4; N = 12.3.  $C_{33}H_{22}O_6N_6S_3$  requires S = 13.8; N = 12.1 per cent.).



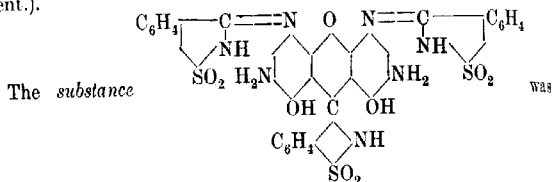
"Saccharin" (3.6 grams), *m*-aminophenol (4.5 grams), and fused zinc chloride (4 grams) were heated at  $180$ – $190^{\circ}$  for two hours. The melt was dissolved in dilute caustic soda and the filtered solution precipitated with hydrochloric acid. The compound, which could not be crystallised, was purified by means of the lead lake, as described in the case of the resorcinol compound. It is a dark brown substance which dissolves in alkali with a brown colour, but without fluorescence. Its solutions in alcohol and acetic acid show a fine moss-green fluorescence (Found: N = 7.2.  $C_{19}H_{14}O_4N_2S$  requires N = 7.6 per cent.).

4 : 4'-Tetramethyldiamino-2 : 2'-oxidophenylsulphamphthalein,



—“Saccharin” (1·8 grams), *m*-dimethylaminophenol (2·8 grams), and fused zinc chloride (1·5 grams) were heated at 180—190° for about one hour, when the melt assumed a deep pink colour and solidified completely. The product was powdered and boiled with alcohol and a little bone black; the filtered solution slowly deposited the condensation product in small, pink needles with a golden lustre.

The substance is very soluble in alcohol, acetic acid, or ether, slightly in water, and dissolves in dilute mineral acids with a pink colour and a strong yellow fluorescence. It dyes fine pink shades on wool (Found: S = 7·5.  $C_{23}H_{23}O_3N_3S$  requires S = 7·6 per cent.).



prepared by heating 1·8 grams of “saccharin,” 4·5 grams of 4 : 6-diaminoresorcinol hydrochloride, and 3 grams of fused zinc chloride at 160° for three hours while a slow stream of dry hydrogen was passed over the molten mass. The cold product was finely powdered, digested with concentrated hydrochloric acid for half an hour, and purified by means of the lead lake. It could not be crystallised. It is a dark brown substance which dissolves in alkali with a splendid blue colour, but without fluorescence (Found: S = 12·8.  $C_{33}H_{23}O_9N_7S_3$  requires S = 12·7 per cent.).

Further work in this direction is in progress.

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CCLXXXIX.—*The Viscosity of Cellulose. Part II. The Lowering of the Viscosity of Cellulose by Various Reagents.*

By REGINALD ARTHUR JOYNER.

It was during the war that the importance became recognised of having cellulose of a definite viscosity, the value of which depended on the use to which the nitrated or acetylated cellulose was to be put. In this vol., p. 1511, was described a modification of the method adopted by Gibson, Spencer, and McCall for the determination of the viscosity in cuprammonium hydroxide, and the effect on the viscosity of varying the concentration of the copper, ammonia, and cellulose was given. The present paper deals with the lowering of the viscosity of cellulose itself by various reagents.

The first definite work published on the effect of solutions of sodium hydroxide on cellulose is given by Gibson (T., 1920, **117**, 479). It was shown that the effect of sodium hydroxide depended on the concentration and the temperature at which the experiment was carried out.

One of the chief difficulties in work on viscosity lies in the interpretation of the results, for example, on p. 2407 is given the effect of increasing amounts of air on the viscosity of cellulose when dissolved in cuprammonium hydroxide. In the second series of experiments, with 2 per cent. solutions of cellulose, it is seen that 2.7, 13.6, and 30 c.c. of air lowered the viscosity by 530, 1300, and 1800 seconds, respectively. Although the lowering of viscosity is relatively great for the first additions of air, it is not correct to assume that the chemical effect is relatively great for the first additions. It was shown in Part I of this paper that the log. viscosity is almost directly proportional to the concentration expressed in grams per 100 c.c. of solvent, and therefore it is clear that if the agent referred to above ultimately reduces the viscosity of the cellulose to a very low figure, then the amount of cellulose transformed will be approximately given by the drop in the log. viscosity. It was shown that celluloses had constants given by a modified Arrhenius formula which were independent of the concentration. Now, the highest viscosity possible for a 2 per cent. solution of cellulose appears to be about 57,000 seconds, or 23,000 absolute units (p. 2399), whilst by repeatedly kieriing a cellulose with sodium hydroxide a viscosity of 1 second for a 5 per cent. solution was obtained. These two figures give constants of 2.78

and 0.15, respectively, which denote the limits for the viscosity of cellulose for a 2 per cent. solution. The hypothesis is now made that there are two kinds of cellulose, high-viscosity cellulose or cellulose "A," which has the higher of the above constants, and low-viscosity cellulose or cellulose "B," which has the lower of the above constants. A cotton which has an intermediate viscosity is a mixture of these two kinds, and the high-viscosity cellulose content will be given by the equation  $x = (\theta - 0.15)/2.63$ , where, by the Arrhenius formula,  $\theta = \log \frac{\text{viscosity of solution}}{\text{viscosity of solvent}} / \text{concentration}$ . In this formula, instead of the log. viscosity of solvent, a number,  $-0.80$ , is used, so that

$$\theta = \frac{\log \text{viscosity of solution} + 0.80}{\text{concentration (gram per 100 c.c. of solvent)}}$$

#### EXPERIMENTAL.

In order to have a standard substance to work with, a large batch of sliver cotton was obtained which gave the following results when tested by routine methods: moisture, 4.62; oily matter, 0.24; mineral matter, 0.71; solubility in 3 per cent. NaOH at 100°, 5.66; copper reduction number,\* 0.11 per cent; dyeing test, nil.

Raw sliver is only partly soluble in cuprammonium hydroxide, but becomes quite soluble after being acted upon by dilute sodium hydroxide, which destroys the protein matter present.

In carrying out the experiments on the action of sodium hydroxide on cellulose, the following procedure was adopted. The cotton was placed in test-tubes, a quantity of the solution of sodium hydroxide or of other substances added, and the cotton worked in the liquid or evacuated to expel the occluded air; the tubes were then filled to a convenient height and sealed. If this procedure be not adopted, the oxygen in the presence of caustic soda will oxidise the cellulose and lower its viscosity. The tubes were then heated in an autoclave at a definite temperature for a definite time. It was found that the temperature of the autoclave could be kept constant to within 1° or 2° for long periods. The autoclave was then opened, the liquor in the tubes titrated, and the cotton washed with dilute acetic acid and thoroughly with water, and finally dried at about 70°. The ratio of liquor to cellulose in the tubes was varied from 15 to 10. The lower ratio could be

\* The copper reduction number is the weight in grams of cuprous oxide reduced by 100 grams of cotton from a solution of the following composition in grams per litre: hydrated copper sulphate 17.3, anhydrous sodium carbonate 100, anhydrous sodium citrate 130. This and the soda-soluble figure give the amount of degraded cellulose present.

decreased considerably without making any difference in the results. Duplicate experiments were often carried out. All the determinations of the viscosity were made at  $20^{\circ} \pm 1^{\circ}$  for a 2 per cent. solution of cellulose, unless otherwise stated.

Table I gives the results obtained when the time of heating was nine hours.

TABLE I.

Showing the effect of varying concentration of sodium hydroxide on sliver cotton when heated for nine hours at the temperatures stated.

100°.			110°		
Normality of NaOH.	Viscosity (sec.).	Cellulose "A."	Normality of NaOH.	Viscosity (sec.).	Cellulose "A."
1.0	5760	81	0.91	2090	73
4.5	1725	71	1.85	1161	68
6.7	425	59	1.84	1203	68
6.7	394	59	2.81	423	60
			3.20	126	49
	125°		3.28	133	49
0.44	950	66	5.49	56	43
0.53	930	66	5.43	53	43
0.96	740	64	6.94	15.6	32
0.96	780	64	6.92	15.4	32
2.92	56	43			
2.92	53	43		134°	
5.52	38	23	0.25	675	62
			0.5	354	58
	141°		1.0	175	52
0.0	350	58	2.0	59	43
0.0	332	58	3.0	9	28
0.17	255	55	4.5	1.4	12
0.17	369	58			
0.44	96	47			
0.43	95	47			
0.90	28	37			
0.86	29	37			

The results shown in Table I have been plotted in Fig. 1, and a series of nearly straight lines is the result. The higher the temperature the more these slope to the left, showing an increasing rate of reaction. These lines, on extrapolation for a zero concentration of sodium hydroxide, cut the abscissa at increasing distances to the left. This denotes that water alone must have some effect on the cotton and that this effect increases rapidly with the temperature.

In order to study the effects of the lower concentrations of caustic soda in more detail, sliver was heated for six and a half hours at  $130^{\circ}$  and a kiered sliver having a viscosity of 314 seconds was heated at the same temperature for five hours. The results are given in Table II.



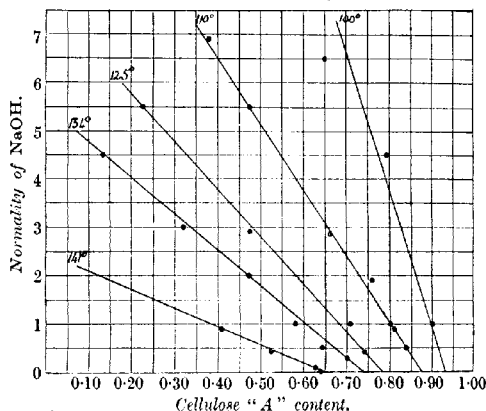
TABLE II.

Showing the effect of low concentrations of caustic soda on sliver when heated at 130° for six and a half hours, and on a kiered sliver, viscosity 314 seconds at 130°, when heated for five hours.

Sliver.			Kiered sliver.		
Normality of NaOH.	Viscosity (sec.).	Cellulose "A" per cent.	Normality of NaOH.	Viscosity (sec.).	Cellulose "A" per cent.
2.17	67, 55	44, 43	2.0	29, 27	37, 37
0.96	105, 126	48, 49	1.0	52, 48	41, 41
0.49	155	51	0.50	57, 50	41, 41
0.24	255	55	0.25	93, 92	42, 42
0.091	336, 358	58, 58	0.10	116, 118	42, 42
0.044	410	59			
Water	415, 476	59, 60	Water	170, 161	43, 43

FIG 1.

Showing the effect of heating sliver with various solutions of sodium hydroxide for nine hours at the temperatures stated.



The results in Table II are shown graphically in Fig. 2, and it is evident the more dilute concentrations of caustic soda have a relatively greater effect than the more concentrated ones. This makes it seem probable that the effect is due to the hydroxyl ions.

The results which have been obtained on the action of sodium hydroxide on cellulose are important from the practical point of view in the kierung of cotton. The concentrations of sodium hydroxide used are generally not more than 4 per cent., and therefore the drop in viscosity can be found for any temperature between 100° and 140° for a kierung period of nine hours. The results for

the various concentrations of sodium hydroxide have been plotted against the temperature in Fig. 3, and it will be seen that when the temperature is lowered the curves become more vertical and approach each other. The extrapolated value of the log. viscosity for the point where they become vertical and touch each other is about 4.75. This means that the maximum value for the viscosity of cellulose is about 57,000 seconds, or 28,000 C.G.S. units at 20° for a 2 per cent. solution in cuprammonium hydroxide containing 13 grams of copper and 200 grams of ammonia per litre.

#### Kinetic Measurements in Presence of Sodium Hydroxide.

Kinetic measurements were carried out, using *N*-sodium hydroxide at various temperatures. In order to eliminate errors due to fluctuating temperature, which would be very difficult to prevent when using an autoclave which could only be heated and cooled slowly, three samples of cellulose having different viscosities were heated for seven hours, simultaneously, at various temperatures. After cooling and washing, the viscosities of the samples were re-determined, and the amount of change, as denoted by the amount of cellulose "A" transformed, was calculated. It is seen that the amount of change in each case is proportional to the amount of cellulose "A" originally present; in other words, the reaction proceeds as though it were unimolecular. The results are given in Table III, *k* hours being calculated for a unimolecular reaction,  $k = 1/t \cdot \log a/a - x$ .

FIG. 2.

Showing effect of heating (1) raw sliver for six and a half hours at 130°, (2) cleaned sliver for five hours at 135°, with different concentration of sodium hydroxide.

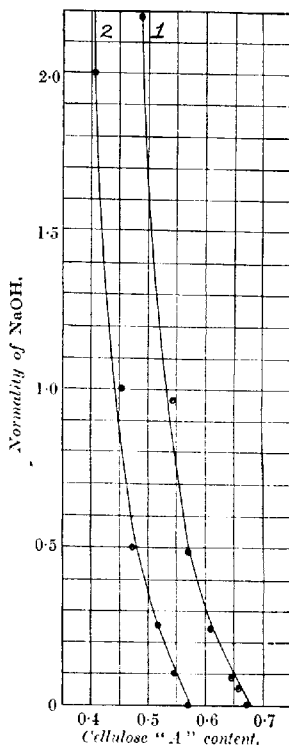
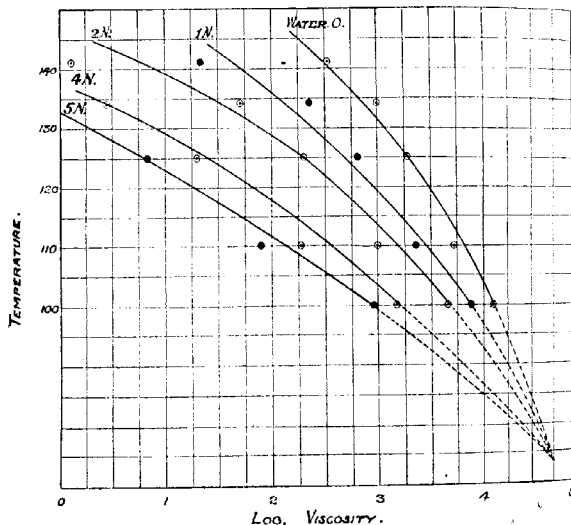


TABLE III.

Showing the calculation of the unimolecular constant,  $k$ , for the action of  $N$ -NaOH on cellulose at various temperatures. Time of heating, seven hours.

Initial viscosity.	Initial cellulose "A" per cent.	Final viscosity.	Final cellulose "A" per cent.	$k$ (hours).	Temp.
1440	69.5	342	57.5	0.0270	116°
240	54.8	84.5	46.1	0.0247	
69	44.5	28.3	37.0	0.0264	
1440	69.5	248	54.8	0.0339	125°
240	54.8	58.2	42.9	0.0340	
69	44.5	23.9	35.6	0.0319	
1440	69.5	67.8	44.2	0.0647	137°
240	54.8	26.2	36.3	0.0589	
69	44.5	10.1	28.6	0.0603	
1440	69.5	10.2	28.6	0.127	146°
240	54.8	6.5	24.8	0.113	
69	44.5	4.6	22.1	0.100	

FIG. 3.



With the exception of the result at the higher temperatures, the constant obtained is fairly satisfactory.

The result found here agrees with many heterogeneous reactions in giving a unimolecular constant, a list of which is given in "A

System of Physical Chemistry," Part I, p. 450, William C. McC. Lewis. As regards the nature of the reaction, the results obtained by Armstrong (*Proc. Roy. Soc.*, 1904, **73**, 508) on the action of enzymes on sugar are of interest. The temperature coefficient for the results with cellulose is low, a rise of  $10^{\circ}$  increasing the rate about 1.6 times, which is in accordance with many results obtained for heterogeneous reactions. This reaction is, however, different from other heterogeneous reactions in that the substance undergoing change is solid, whilst the catalyst is a liquid. From these results it is now possible to state the conditions necessary in order to lower the viscosity of cellulose of any viscosity by a required amount.

In the last experiment, along with the three samples of cleaned sliver a sample of raw sliver was also subjected to the action of *N*-sodium hydroxide, and thereafter the viscosity was determined. Knowing, therefore, the final amount of cellulose "A," and using the constants obtained, it was possible to calculate the amount of cellulose "A" in the pure unattacked sliver. The average values for the constant being employed in each case, except in the last, where the highest one was used, the values found were 86, 86, 82, and 83 per cent. The actual values should have been 100 per cent. in each case.

*The Selective Sorption of Sodium Hydroxide by Cellulose and its Action in lowering the Viscosity.*

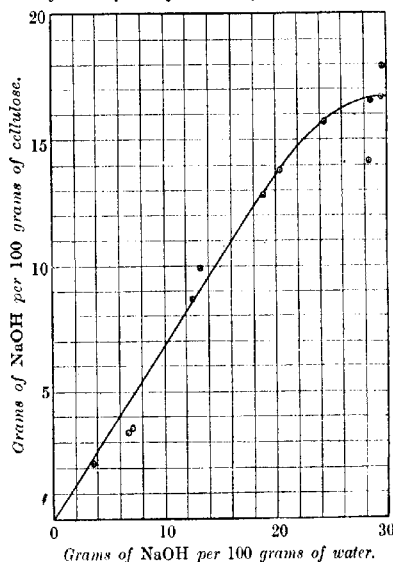
With solutions stronger than normal, the action of sodium hydroxide in lowering the viscosity has been shown to be nearly proportional to the gross concentration of the sodium hydroxide. Although this was probably accidental, depending on various factors, for example, degree of ionisation, hydration, etc., it was thought interesting to study the action from the sorption point of view, as it was known that the sorption of sodium hydroxide from aqueous solution by cellulose also increases with the concentration.

The question of the sorption of sodium hydroxide by cotton has been revised by Leighton (*J. Physical Chem.*, 1916, **20**, 32) especially from the point of view of the phase rule, and it was shown that the occurrence of definite combination between cellulose and sodium hydroxide has by no means been proved. Leighton showed that measurements involving decrease in concentration of a sodium hydroxide solution due to the addition of cotton give simply the amount of selective sorption, that is, the difference in the absorption of sodium hydroxide and water. He endeavoured to measure the total sorption by centrifuging cotton which had been placed in

sodium hydroxide solution; on the assumption that the cotton had then no solution clinging to it, the increase in weight of the cotton and the amount of sodium hydroxide therein gave the quantity of water and of sodium hydroxide sorbed. This method obviously furnished too high results, because from his experiments he deduced that 1 gram of cotton can sorb 4 grams of water, whilst in reality wet cotton can be squeezed so that the water content falls as low as 0.8 gram per gram of cotton.

FIG. 4.

Showing the sorption of sodium hydroxide by cellulose.



Vieweg (*Ber.*, 1907, **40**, 3876) determined the selective sorption of sodium hydroxide from an aqueous solution by titrating a definite volume of solution before and after the addition of cotton. In the present work, in order to obtain more accurate results the analyses were done on definite weights of the solutions. Known weights of sodium hydroxide (volume 10 c.c.) and cellulose (about 1 gram) were well mixed together at room temperature and a definite weight of the solution was titrated. Preliminary experiments showed that after one and a half hours the selective sorption of the sodium hydroxide did not increase in six days. The results obtained are shown in Table IV and graphically in Fig. 4.

TABLE IV.

Giving results obtained for the selective sorption of sodium hydroxide by cotton.

Composition of aqueous phase.				Composition of cellulose phase.	
Grams of NaOH per 100 grams of water.				Grams of NaOH per 100 grams of cellulose.	
			29.6	16.6, 17.8	
			28.6	14.1, 16.5	
			24.3	15.7	
			20.5	13.9	
			19.1	12.8	
			18.8	12.6, 12.8	
			13.3	9.9	
			12.8	8.6	
			7.65	3.41	
			6.95	3.23	
			4.02	1.72	
			3.79	2.20, 2.27, 2.15, 2.12, 2.01	

These results show that sorption of sodium hydroxide by the cellulose takes place. This sorption, as will be seen, is increased by the addition of neutral salts.

Preliminary experiments on the effect of the addition of sodium chloride to the sodium hydroxide solution showed that the concentration in the cellulose phase increased, and accordingly solutions were made by adding increasing amounts of sodium chloride to sodium hydroxide. In these solutions the ratio of water to sodium hydroxide was therefore constant. The sorption from these solutions was determined and also the effect on sliver after heating for six and a half hours at 122°.

TABLE V.

Showing the effect of adding increasing amounts of salt on the sorption of sodium hydroxide by cellulose, and the relative effects of such solutions on cellulose.

Composition of solution.				Grams of NaOH per 100 grams of cellulose.	Viscosity (sec.).	Cellu. loss "A."
NaOH.	Percentage of NaCl.	Percentage of NaNO <sub>3</sub> .	water.			
7.1	—	—	92.9	76.5	3.41	433, 414
6.5	6.8	—	86.7	73.5	5.11	482
6.0	13.6	—	80.4	70.2	5.40	417
5.3	22.4	—	72.3	65.0	5.95	388
4.2	13.7	23.1	59.0	56.0	6.40	111, 108

The effect of other neutral salts was studied and it was found that neutral salts alone had little effect on raw sliver at 120°, but in conjunction with sodium hydroxide potassium chloride had a

specially strong effect. When, however, a sliver which had already been acted upon by sodium hydroxide was so treated, potassium chloride had an effect almost equal to that of an equivalent concentration of sodium or potassium hydroxide, whilst the effect of sodium chloride, sodium nitrate, barium chloride, or potassium nitrate was almost negligible at 120°. As was stated on p. 2396, raw sliver is not very soluble in cuprammonium hydroxide, and it would seem that in its natural state it contains very little free cellulose and that the protein matter must first of all be destroyed before the cellulose can be attacked.

Further results on the effects of sodium and potassium chlorides are given in Table VI.

TABLE VI.

Showing the effect of equivalent concentrations of potassium chloride and sodium chloride on sliver in seven and a half hours at 120°.

Composition of solution.	Viscosity.	Cellulose "A" per cent.
(a) 2N-NaOH	340, 326	57
(b) 2N-KOH	510, 491	61
100 c. c. of (a) with 20 grams of KCl	72, 71	45
" " " 15.9 " NaCl	445, 431	59
" " (b) " 20 " KCl	82, 82	46
" " " 15.9 " NaCl	652	63

These results confirm the others as regards the relative effects of sodium chloride and potassium chloride. The effect of the potassium chloride may be due to its slightly increasing the hydroxyl-ion concentration, also to its raising the potential of the hydroxyl ions; it may also have a specific action on the cellulose.

It was found that the sorption of sodium chloride or potassium chloride by cellulose from 22 per cent. solutions was small, being only about 1 gram per 100 grams of cellulose.

When sliver was heated with a solution of ammonium chloride or calcium chloride, a degraded product of very low viscosity resulted, but when a mixture of ammonium chloride and ammonia was used, there was scarcely any effect. Evidently the action of the ammonium chloride or calcium chloride was due to the acid set free by hydrolysis. Ammonia solution alone also had little action.

#### *The Action of Dilute Acids on Cellulose.*

It was recognised that the action of dilute acids on cellulose was much more rapid than that of alkalis, but on account of their degrading action it was necessary to use such a strength that little or no hydrocellulose could be formed.

The following tables show the action of various strengths of hydrochloric acid in degrading cellulose at 100°.

TABLE VII.

Showing the action of various strengths of hydrochloric acid on cellulose at 100°.

Strength of acid.	Time of action.	Remarks.
N/1HCl	5 minutes	Converted to powder.
"	55 "	50% of the product soluble in 3% NaOH; viscosity of 5% sol. = 1 sec.
N/10HCl	10 "	Soluble in NaOH, 4 per cent.
"	30 "	" " 12 "
N/30HCl	30 "	" " 4 "
"	3 hours	" " 12 "
N/100HCl	3 "	" " 3 "

The experiments with acids were therefore limited to concentrations of N/30 and N/100.

In determining the rate of reaction, cellulose was boiled under reflux, at a definite time cold water was poured down the condenser to stop the reaction, and the product was well washed and dried at 70°. The viscosity, usually for a 2 per cent. solution, was determined; the percentage of cellulose "A" and the constants  $k$  for the various orders of reaction were calculated:  $k_{\text{uni}} = \frac{1}{t} \log \frac{a}{a-x}$ ;  $k_{\text{bi}} = \frac{1}{t} \left( \frac{1}{a-x} - \frac{1}{a} \right)$ ;  $k_{\text{ter}} = \frac{1}{2t} \left( \frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$ , where  $a$  = fraction of cellulose "A" at time 0 and  $a-x$  = fraction at time  $t$  minutes.

TABLE VIII.

Showing the effect of dilute hydrochloric acid on cleaned cellulose.

Time in min.	Viscosity in sec.	Fraction of cellulose "A."	$k_{\text{uni}}$	$k_{\text{bi}}$	$k_{\text{ter}}$	Remarks.
—	1480	0.697	—	—	—	
5	115	0.481	0.054	0.13	0.22	Acid N.100HCl.
10	59	0.431	0.048	0.089	0.16	T = 100°.
20	18.0	0.333	0.038	0.078	0.18	Cellulose sliver.
30	11.8	0.298	0.028	0.064	0.15	Solubility in NaOH at
55	3.5	0.198	0.023	0.065	0.22	end, 3%.
175	1.2	0.110	0.011	0.044	0.23	
—	1480	0.697	—	—	—	
5	132	0.498	0.065	0.11	0.20	Acid 0.0113N-HCl.
10	57	0.427	0.048	0.090	0.17	T = 100°.
20	17.7	0.332	0.036	0.079	0.18	Cellulose sliver.
30	8.9	0.276	0.030	0.071	0.18	
45	5.0	0.228	0.024	0.066	0.18	
60	3.7	0.204	0.020	0.057	0.18	Solubility in NaOH at end, 1%.



TABLE VIII (continued).

Time in min.	Viscosity in sec.	Fraction of loss "A."	$k_{\text{ter}}$	Remarks.	Time in min.	Viscosity in sec.	Fraction of loss "A."	$k_{\text{ter}}$	Remarks.
0	1480	0.697	—	Acid 0.286N.	0	1480	0.697	—	Acid
5	83.5	0.358	0.56	HCl. T = 100°.	15	727	0.638	0.0130	0.0100N.
10	22.0	0.269	0.58	2.5% for viscosity	45	395	0.589	0.0092	HCl. T = 80°.
20	12.5	0.232	0.41	except at 165	105	198	0.531	0.0070	80°.
30	6.6	0.190	0.43	zero time.	165	105	0.478	0.0070	
60	2.1	0.117	0.59	Sliver.	285	47	0.411	0.0067	Sliver.
120	0.9	0.058	1.20		405	32.6	0.382	0.0059	
					405	29.3	0.374	0.0054	
0	224	0.491	—	Acid	0	840	0.650	—	Acid
5	72	0.405	0.19	0.0100N-HCl.	1	485	0.606	0.18	0.0100N.
10	45	0.368	0.16	T = 100°.	4	197	0.530	0.15	HCl.
20	18.2	0.300	0.17	Linters	19	30.0	0.391	0.11	T = 100°.
30	12.5	0.270	0.16	2.5% for vis-					
60	5.1	0.196	0.18	cosity.	59	5.4	0.232	0.14	Cops.
150	2.7	0.152	0.13						

It is seen that  $k_{\text{ter}}$  is fairly constant. As the concentration of the acid remains constant throughout the reaction, the number denoting the order should be increased by one, and if the reaction took place in a homogeneous phase giving a termolecular constant, the reaction would be strictly quadrimolecular. However, in view of the fact that the reaction is apparently heterogeneous it is difficult to imagine that the obtaining of the constant has the same significance as it would have if the reaction took place in a homogeneous liquid phase. The temperature effect is large and it appears that the constant is probably proportional to the acid concentration. One experiment was made with acetic acid, when an *N*/10-solution in fifty minutes reduced the viscosity of a cellulose from 1480 seconds to 68 seconds. *N*/100-Hydrochloric acid would take about ten minutes to produce the same lowering. An *N*/10-solution of acetic acid has about twice the effect expected from a comparison of the concentration of the hydrogen ions in *N*/100-hydrochloric acid.

#### *Reduction of the Viscosity of Cellulose by Oxidising Agents.*

The first experiments under this heading were made with cellulose in cuprammonium solution. The viscosity was first determined in an atmosphere of hydrogen. After one-quarter of the cellulose solution had run out, to the remainder a measured volume of air was added and the mixture well shaken for an hour, the reaction being half complete in five minutes. Blank experiments were carried out on the hydrogen from time to time. The results obtained are shown in Table IX.

TABLE IX.

The quantitative effect of air on the lowering of the viscosity of cellulose cuprammonium solutions.

Seventy-five c.c. of solution were used in each experiment.

2 Per cent. solution of cellulose.						
1	2	3	4	5	6	
Viscosity before.	Cellu- lose "A" before.	Viscosity after.	Cellu- lose "A" after.	C.c. air added.	Diff. in cellul- lose "A" per c.c. of air.	Column 6, Column 2.
242	0.547	17.1	0.329	20.7	0.0105	
240	"	7.2	0.258	25.1	0.0114	
245	0.548	4.8	0.226	30.7	0.0105	
				Mean	0.0108	0.020
1420	0.694	890	0.656	2.7	0.0140	
1400	"	73	0.449	13.6	0.0180	
1790	0.713	27	0.367	21.2	0.0164	
1840	0.715	5.0	0.238	30.2	0.0158	
				Mean	0.0161	0.023
67.4	0.443	43.0	0.405	3.9	0.0097	
66.4	"	27.0	0.368	8.5	0.0087	
70.0	0.447	10.1	0.286	16.4	0.0098	
72.8	0.450	4.7	0.223	25.6	0.0101	
				Mean	0.0096	0.021
4 Per cent. solution of cellulose.						
2950	0.375	1850	0.348	6.3	0.0043	
1680	0.333	512	0.283	15.9	0.0039	
2730	0.354	220	0.249	32.5	0.0032	
				Mean	0.0035	0.010
1 Per cent. solution of cellulose.						
34.6	0.841	21.4	0.761	3.4	0.0225	
34.4	"	9.6	0.627	9.9	0.0217	
33.0	0.836	3.7	0.472	16.6	0.0219	
34.2	0.837	1.5	0.319	27.7	0.0186	
				Mean	0.0212	0.025

The viscosity values show that the addition of a small amount of air brings about a great change, whilst further additions produce little effect. When, however, the content of the hypothetical cellulose "A" is considered, the effect of the air is, for cellulose of the same viscosity, roughly proportional to the amount added.

As was mentioned in Part I of this paper, oxygen reacts somewhat slowly with cuprammonium solution and produces nitrite, but it was proved during the present work that it is not the oxygen which so reacts which reduces the viscosity of cellulose, but that the reaction is direct. From the relative speeds of the two reac-

tions it would seem that most of the oxygen, when introduced into a cuprammonium solution, reacts with the cellulose.

From the above figures it is possible to calculate roughly the amount of oxygen necessary to reduce the viscosity of cellulose to its lowest limit, in other words, to convert all the cellulose "A" to cellulose "B." This amounts to about 5.3 c.c. per gram at *N.T.P.*, which means that 16 grams of oxygen react with about 2100 grams of cellulose. It will be seen that a similar figure is obtained in the experiments with sodium hypochlorite.

#### *Experiments on Undissolved Cellulose.*

It was noticed that the lowering of the viscosity of cellulose during the kieren operation was in general considerably greater than would have been expected from the results of autoclave experiments carried out under the same conditions of temperature and concentration of sodium hydroxide. The cause of this was found to be the air in the cotton, for when the cotton was thoroughly wetted and steamed before the caustic soda was added the cleaned cellulose had a much higher viscosity than that measured when no such precautions had been taken.

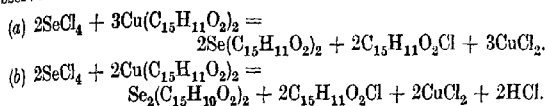
It was found that by simply boiling cellulose with 4 per cent. caustic soda for three-quarters of an hour at atmospheric pressure, during which time hydrogen peroxide was added, the viscosity was reduced from 2160 to 1.7 seconds. The cellulose had no copper reduction number and therefore it was evident that by this means the viscosity of cellulose could be lowered without the cellulose being appreciably degraded.

Experiments were then made using sodium hypochlorite instead of hydrogen peroxide. It is known that in acid solution cellulose is quickly attacked by chlorine ("Cellulose," 1918 edition, Cross and Bevan, p. 59). It was found that, when boiled with 4 per cent. sodium hydroxide and much hypochlorite, cellulose was rapidly disintegrated to a powder of very low viscosity. On further boiling, the powder became finer, and on being washed with water, swelled up. The powder was partly soluble in water, but was reprecipitated by sodium sulphate solution. It was noticed that during this boiling a yellow colour would suddenly appear; this indicated that all the hypochlorite had been used up, for the colour vanished on the addition of more of the reagent. By this means it was possible to oxidise cellulose almost entirely to carbon dioxide. When sugar was employed instead of cellulose, the same phenomenon was observed, and when the yellow colour appeared formaldehyde was detected by its odour.

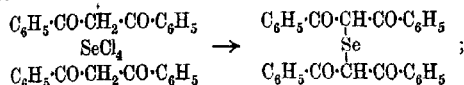
It was found that by the addition of about 1.5 c.c. of *N*-sodium

IV. *Selenium Tetrachloride and Copper Dibenzoylmethane.*

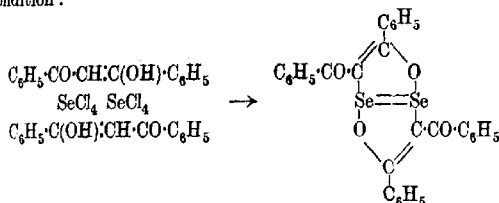
The case of copper dibenzoylmethane has given rise to remarkably well-defined, stable selenium derivatives, so that the selenium tetrachloride condensation stands in marked contrast to the tellurium tetrachloride reaction with dibenzoylmethane, which yielded only an unstable hydrolysable product. The following changes were observed :



In the simpler reaction, *selenium bisdibenzoylmethane* (XXIII) is produced as follows :



whilst in the more complex condensation, two molecules of selenium tetrachloride take part, giving rise to *selenium dibenzoylmethane* (XXV), which, like selenium acetylacetone, exists in the dimeric condition :

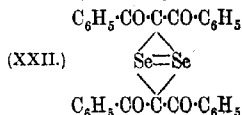


The axially symmetric structure is assigned to selenium dibenzoylmethane because it behaves towards hydrocyanic acid and towards hydriodic acid in a manner analogous to that of selenium acetylacetone (compare p. 2436), forming, respectively, the colourless monomeric *cyano-selenium dibenzoylmethane* (XXIV) and the orange dimeric *diselenium bisdibenzoylmethane* (XXVIII).

An isomeric form of selenium dibenzoylmethane is produced together with a small proportion of selenium dibenzoylmethane by the regulated heating of selenium bisdibenzoylmethane, two molecules of which condense with the elimination of two molecules of dibenzoylmethane. To this isomeric substance, *isoselenium dibenzoylmethane*, is assigned the plane symmetric formula (XXVI), since, on further heating or under the catalytic influence of hydrogen cyanide or of hydriodic

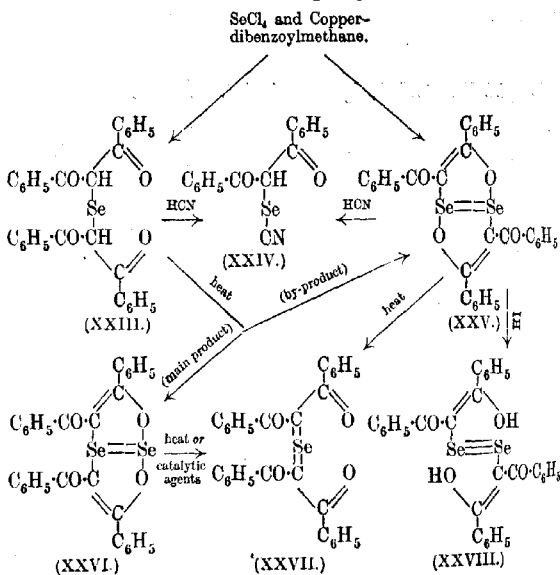
acid, it readily loses an atom of selenium and passes quantitatively to an orange compound, *selenium dehydrobisdibenzoylmethane* (XXVII). The latter, formed also in quantitative yield together with selenium by melting selenium dibenzoylmethane, is a well-defined and remarkably stable compound, which, unlike all the other selenium derivatives of this series, is not attacked by excess of hydriodic acid.

It should be remarked, however, that the formula



is not entirely excluded as a representation of the structure of isoselenium dibenzoylmethane, this and the formula XXVI being related somewhat in the manner of keto- and enol-forms of the same substance. The structure XXII may well represent an intermediate phase in the degradation of each of the two isomeric selenium dibenzoylmethanes to selenium and selenium dehydrobisdibenzoylmethane by means of heat.

These selenium compounds of dibenzoylmethane are of especial interest on account of their close genetic relationships, an aspect which is illustrated in the following diagram:



## EXPERIMENTAL.

## I. Preparation of Selenium Acetylacetone from Copper Acetylacetone.

The following method is a convenient variant of the processes outlined in earlier communications (T., 1920, 117, 1459; 1921, 119, 1067).

Twenty-five grams of powdered copper acetylacetone (1 mol.) were added during fifteen minutes to 20.5 grams of selenium tetrachloride (1 mol.) suspended in 120 c.c. of chloroform freed from alcohol, the reaction being moderated by cooling in ice and salt. Copper chloride was removed, after thirty minutes at the ordinary temperature; the chloroform solution was evaporated in a stream of air, when the solvent and chloroacetylacetone were removed and 11.3 grams of pure selenium acetylacetone were left (calculated amount = 16.4 grams) (Found: Se = 44.65.  $C_{10}H_{12}O_4Se_2$  requires Se = 44.68 per cent.).

This preparation was varied (selenium tetrachloride 1 mol., copper acetylacetone  $1\frac{1}{2}$  mol.) in order to ascertain whether a *cyclo-triselenium* derivative (pp. 2439, 2467) was formed, but only selenium acetylacetone was found on working systematically through the product.

In repeating this preparation, it was noticed that the weight of copper chloride was invariably greater than that demanded by equation (a) on page 2433. By working in B.P. chloroform (100 c.c.) with 21.2 grams of selenium tetrachloride and 25.1 grams of dry copper acetylacetone, 17 grams (78 per cent.) of selenium acetylacetone were obtained and 17.1 grams of precipitated copper chloride (calculated, 12.9 grams of  $CuCl_2$ ). The excessive amount of this precipitate is due to: (1) hydration of copper chloride in the air, (2) red selenium and other ill-defined products, (3) occluded chloroform and chloroacetylacetone.

Selenium acetylacetone was not affected by methyl or ethyl iodide, acetone, or acetonitrile. It crystallised unchanged with great facility from the last of these reagents. Hydrogen chloride in dry ether dissolved selenium acetylacetone, but had no further action on the selenium compound; hydrochloric acid led to the formation of an unstable additive compound, soluble in ether, which decomposed into selenium and chloroacetylacetone. This decomposition occurred more rapidly in alcoholic hydrochloric acid. Anhydrous ammonia, when sealed up with selenium acetylacetone, decomposed the latter completely. The identified products were selenium, acetamide, and hydrocyanic acid. The presence of the last substance recalled the formation of carbylamines by the

interaction of aromatic primary amines and selenium acetylacetone (T., 1921, 119, 622).

*Description of the Crystalline Forms of Selenium Acetylacetone.*

This substance crystallises in two distinct modifications. Both forms are somewhat elongated, six-sided plates, which are not suitable for measurement on the goniometer. Under the microscope, the first form is seen to have a symmetrical dome-termination of  $88^\circ$ . Optically, the extinction is straight, and a negative acute bisectrix is normal to the plate. The axial angle is wide. The system is therefore almost certainly orthorhombic. The second form, on the other hand, is probably monoclinic, for the termination is unsymmetrical with angles of  $56^\circ$ ,  $51^\circ$ , and  $73^\circ$ , the extinction is oblique, and a positive acute bisectrix is normal to the plate—which must therefore be the face  $b(010)$ . On recrystallising from benzene at suitable concentration, the second form suffers a transformation into the first.

*Diselenium Bisacetylacetone (Formula VII).*

1. *Preparation from Selenium Monochloride and Copper Acetylacetone.*—The selenium monochloride used in these experiments was prepared by dissolving the calculated amount of selenium in selenium tetrachloride. The monochloride (9.3 grams), dissolved in 40 c.c. of chloroform B.P., was added with shaking to 10.7 grams of copper acetylacetone in 150 c.c. of the same solvent, the mixture being cooled to  $0^\circ$ . The colour of the copper acetylacetone disappeared before all the selenium chloride was added, and a red precipitate ( $a = 9.5$  grams) separated, which was collected after one hour. The filtrate after evaporation to remove chloroform left a dark yellow, lachrymatory oil ( $b = 9.8$  grams).

The product  $a$  on treatment with water was found to consist of red selenium, cupric chloride, and a complex double salt of copper chloride and the organo-selenium compound which dissociated in a mixture of water and chloroform into soluble cupric chloride and a copper compound of diselenium bisacetylacetone, the latter dissolving readily in the organic solvent to a green solution, from which the copper derivative (2 grams) was recovered on evaporation. From this copper compound dissolved in chloroform, diselenium bisacetylacetone was obtained by shaking with dilute sulphuric acid. The chloroform layer gave a yellow oil, which solidified partly to orange crystals identical with those obtained by the second method of preparation. The oil  $b$ , on extraction with light petroleum, yielded a further amount of diselenium bisacetylacetone. The

glutinous residue contained more of this substance together with selenium acetylacetone and a trace of chloroacetylacetone.

When the preparation was varied by adding the copper acetylacetone solution to that of selenium monochloride until the blue colour was no longer discharged (21.7 grams of copper salt in 240 c.c. of chloroform to 16.5 grams of  $\text{Se}_2\text{Cl}_2$  in 100 c.c. of  $\text{CHCl}_3$ ), about half the selenium was set free, the remaining products being diselenium bisacetylacetone, a complex organic copper salt, selenium acetylacetone, anhydrous cupric chloride, red selenium, and traces of chloroacetylacetone.

2. *Preparation from Selenium Acetylacetone and Hydriodic Acid.*—Powdered selenium acetylacetone (5.5 grams) was added during ten minutes to a cooled and shaken mixture of 150 c.c. of ether, 5 c.c. of decolorised 60 per cent. hydriodic acid, and 100 c.c. of water. The ethereal layer was washed with water, the iodine removed by 340 c.c. of *N*/10-sodium thiosulphate (calculated = 311 c.c.); the intense orange-yellow ether layer, after filtering from red selenium, was evaporated to remove solvent and a small amount of acetylacetone, leaving orange crystals of diselenium bisacetylacetone (3.9 grams).

3. *Preparation from Selenium Tetrachloride and Copper Acetylacetone.*—To 5 grams of selenium tetrachloride (1 mol.), suspended in 50 c.c. of dehydrated chloroform B.P. cooled to  $0^\circ$ , were added all at once 11.8 grams of dry copper acetylacetone (2 mols.). After two hours the greenish-black precipitate (*a*) was collected, the brownish-orange filtrate yielding chloroacetylacetone and 1.3 grams of selenium acetylacetone. The precipitate (*a*), which was quite insoluble in chloroform, was decomposed by water into copper chloride and 3.1 grams of a greenish-yellow powder, now readily soluble in cold chloroform. The solution in this solvent, when shaken with dilute sulphuric acid to remove combined copper, left on evaporation a yellow oil containing chloroacetylacetone. Extraction of this oil with light petroleum yielded diselenium bisacetylacetone, separating in well-defined, orange crystals identical with the other two preparations.

The products from the three preparations, when crystallised from light petroleum, separated in six-sided plates or prisms having a bright orange colour and a farinaceous and burnt rubber odour, which was nearly lost on drying. In the majority of cases, the compound began to soften at  $78^\circ$  and melted at  $92-93^\circ$ , but occasionally purified specimens softened at  $58^\circ$  and melted at  $8-80^\circ$ .

The variations in melting point indicate the existence of interconvertible forms. These modifications, having possibly mono-



and di-enolic structures, would furnish different copper salts, one of which might be the compound soluble in chloroform whereas the other is insoluble in this solvent.

Diselenium bisacetylacetone was readily soluble in the organic solvents, but insoluble in cold water. In warm alcoholic solution, the compound was decomposed, giving red selenium, acetylacetone, and a yellow oil; this change occurred more slowly in the cold. Molecular weight cryoscopically in benzene ( $c = 2.674$ ), found  $M = 339$ ;  $C = 33.61$ ;  $H = 4.01$ ;  $Se = 44.30$ .  $C_{10}H_{14}O_4Se_2$  requires  $M = 356$ ; and  $C = 33.67$ ;  $H = 3.96$ ;  $Se = 44.43$  per cent.

The compound differs by only two hydrogen atoms from selenium acetylacetone, and this difference is clearly shown in the respective analyses (T., 1920, 117, 1460). Of the foregoing preparations the hydriodic acid method (No. 2) gives the best yield of diselenium bisacetylacetone.

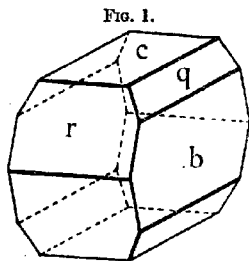


FIG. 1.

Diselenium bisacetylacetone and dry ammonia in ethereal solution gave a yellow precipitate probably of ammonium salt very easily decomposed by atmospheric moisture; 5*N*-sodium hydroxide dissolved the compound to a yellow solution from which selenium was speedily liberated. Hydrazine hydrochloride and phenylhydrazine eliminated selenium in acetic acid and alcoholic solution,

respectively. Aqueous potassium hydrogen sulphite reacted very slowly with this diselenium compound dissolved in ether. After three days, the change was incomplete and the products consisted of potassium selenodithionate, red selenium, sulphur dioxide, and acetylacetone. Ferric chloride gave instantaneously an intense red coloration.

The crystals of diselenium bisacetylacetone prove to be isomorphous with the corresponding dithio-compound prepared by Angeli and Magnani, and described by Negri (*Gazzetta*, 1893, 23, [ii], 445). The system is orthorhombic with  $a:b:c = 0.954:1:1.727$ , the forms developed being  $c(001)$ ,  $q(011)$ ,  $b(010)$ , and  $r(101)$ , as shown in Fig. 1, with occasional traces of  $s(012)$ . Following are the mean values obtained by the measurement of two crystals.

	$c(001)$ .	$q(011)$ .	$b(010)$ .	$r(101)$ .	$s(012)$ .
$\phi$ .....	polar	$0^\circ 0'$	$0^\circ 0'$	$89^\circ 53'$	$0^\circ 0'$
$p$ .....	face	$59.56$	$90.0$	$61.7$	ca. $40^\circ$

Fedorov complex-symbol;  $(4d)59(-\frac{1}{2})$ ; trans.  $110/\bar{1}10/001$ .

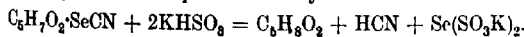
Cleavage, *c* perf. and showing pearly lustre. Acute positive bisectrix (with medium angle) perpendicular to *b*; axial plane *c*(001).

*Copper diselenium bisacetylacetone* (Formula VIII) was prepared by shaking a benzene solution of the diselenium compound with excess of aqueous cupric acetate with or without the calculated amount of ammonia; the yellow copper derivative, which was precipitated quantitatively, was washed with water and benzene. This copper compound was insoluble in water, petroleum, or acetone, and only sparingly soluble in benzene or chloroform, thereby differing from the copper derivative formed in the first preparation (p. 2445) the latter being readily soluble in chloroform. Copper diselenium bisacetylacetone reddened at 130—135° and decomposed with blackening between 150—170°; it dissolved in cold 5*N*-sodium hydroxide to a yellow solution, which changed successively to red and black (Found: Se = 38·83, 38·02; Cu = 15·52.  $C_{10}H_{12}O_4Se_2Cu$  requires Se = 37·89; Cu = 15·21 per cent.).

*Cyano-3-selenium Acetylacetone* (Formula IX).

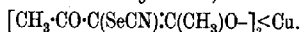
Powered selenium acetylacetone (3 grams) was added to 10 c.c. of freshly distilled hydrogen cyanide diluted with an equal volume of dry ether at 0°, the mixture being shaken at intervals for fourteen hours. The crystalline deposit was then completely soluble in cold ether, no unchanged selenium acetylacetone being present. The ether and hydrogen cyanide were removed under reduced pressure. With pure hydrogen cyanide free from polymerides and phosphoric acid, the yield of selenocyanate was quantitative. When crystallised from warm light petroleum (b. p. 40—60°), *cyano-3-selenium acetylacetone* separated in brittle, colourless needles which acquired a stouter habit as growth proceeded in the cooled solutions; these crystals softened at 75° and melted at 78—80° to a colourless liquid. The compound, which had an unpleasant odour resembling that of burnt indiarubber, was highly sternutatory and on long exposure to light and air it became brownish-pink and emitted a faint odour of hydrogen cyanide, being ultimately transformed to a brittle, red mass [Found: C = 35·71; H = 3·81; N = 7·09; Se = 38·20, 38·41. In benzene (*c* = 1·426) by the cryoscopic method, *M* = 197.  $C_6H_7O_2NSe$  requires C = 35·26; H = 3·46; N = 6·86; Se = 38·76 per cent.; *M* = 204].

Cyano-3-selenium acetylacetone dissolved freely in alcohol, benzene, or chloroform, more sparingly in ether; almost insoluble in cold water, it was decomposed on boiling. With upwards of two molecular proportions of aqueous potassium hydrogen sulphite, the selenocyanate decomposed smoothly as follows:



The selenium was obtained almost wholly as potassium selenodithionate, only traces of the element being formed. With one molecular proportion of the bisulphite, the products were acetylacetone, potassium hydrogen sulphate, hydrogen cyanide, and selenium.

*Copper Cyano-3-selenium Acetylacetone,*



The enolic character of the selenocyanate was manifested by its red coloration with aquo-alcoholic ferric chloride and by the formation of a copper derivative on shaking together excess of aqueous 5 per cent. copper acetate (3 equivalents) and selenocyanate dissolved in 25 parts of chloroform or benzene. The light blue copper compound, almost insoluble in chloroform or benzene, was precipitated in the aqueous layer, shaken up again with more copper acetate, and then dried to constant weight over calcium chloride (Found: Se = 33.06; Cu = 13.79.  $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_2\text{Se}_2\text{Cu}$  requires Se = 33.69; Cu = 13.53 per cent.). The copper compound was insoluble in water, benzene, acetone, or alcohol; boiling chloroform was slightly tinted. It was decomposed by acetic acid or aqueous sodium hydroxide.

*Selenium OC-Bisacetylacetone (Formula I).*

Selenium OC-bisacetylacetone, produced by heating under reflux one part of selenium acetylacetone with 3 parts of acetylacetone and 6 parts of ethyl alcohol, was obtained after spontaneous evaporation to dryness in a vacuum over quicklime. It was prepared also in quantitative yield by refluxing selenium acetylacetone with 3 parts of acetylacetone and 11 parts of chloroform. The course of this additive change was, however, influenced in a remarkable degree by traces of impurity, for although it sometimes occurred in chloroform purified through the salicylide compound, yet in other cases the reaction was incomplete even after prolonged boiling. Addition of a small proportion of ethyl alcohol sometimes brought this change to completion, but when this procedure failed the reaction was facilitated by adding either excess of acetylacetone or a trace of solid sodium hydroxide. Non-reactive forms of selenium acetylacetone became reactive when crystallised from alcohol or benzene. Microscopic examination of the inert and reactive forms showed, however, no differences in crystalline form.

Selenium OC-bisacetylacetone was also obtained in an attempt to prepare the isomeric selenium CC-bisacetylacetone by shaking together in 45 c.c. of cold dehydrated chloroform B.P. 1.1 grams of selenium tetrachloride (1 mol.) and 5.3 grams of dry copper

acetylacetone (4 mols.). After two hours, the dark green precipitate was decomposed by water, when cupric chloride dissolved and 1.6 grams of unaltered copper acetylacetone containing a little copper chloroacetylacetone was recovered. The dark green chloroform filtrate, after shaking with dilute sulphuric acid to remove combined copper, left on evaporation a yellow oil which deposited colourless needles of selenium *OC*-bisacetylacetone, whilst the mother-liquor, on the addition of alcohol, yielded selenium acetylacetone.

In aqueous sodium hydroxide the bisacetylacetone compound dissolved to a bright yellow solution which became red, developing a nauseating odour and liberating selenium. These changes occurred more slowly with sodium hydrogen carbonate. The substance was acid to moist litmus paper, and in dry ether it reacted slowly with metallic sodium, giving a yellowish-white sodium derivative. Dry ammonia added to the ethereal solution gave a yellow precipitate of an unstable ammonium salt. Ferric chloride gave an intense red coloration. The substance was decomposed by warming with alcoholic solutions of pyridine, aniline, or *p*-nitro-phenylhydrazine.

The reaction of selenium *OC*-bisacetylacetone with aqueous potassium hydrogen sulphite (2 mols.) occurred in two stages, half the calculated amount of acetylacetone only being eliminated initially. After extracting this product with chloroform, the colourless solution, on warming with alcohol, yielded potassium selenodithionate and the remainder of the acetylacetone.

Selenium *OC*-bisacetylacetone dissolved readily in cold ether, ethyl iodide, chloroform, benzene, or toluene; and when crystallised from light petroleum it separated at first in fluffy masses of colourless, prismatic needles having, while moist, a marked farinaceous odour. These needles, which were not suitable for crystallographic investigation, retained their form when collected, but if left in the mother-liquor they became completely transformed in two to eight days into a more compact form, fully described below. Both forms, when rapidly heated, melted at 50–54° to a colourless liquid becoming cloudy owing probably to separation of selenium acetylacetone. When heated slowly, these preparations softened at 42° owing to the beginning of dissociation. The molecular weight determined in benzene cryoscopically was 283 ( $c = 2.68$ ), 288 ( $c = 3.75$ ). The analyses gave C = 43.22; H = 5.19; Se = 28.14, 28.19, 28.49, 28.13.  $C_{10}H_{14}O_4Se$  requires  $M = 277$ ; and C = 43.28; H = 5.09; Se = 28.56 per cent.

Selenium *OC*-bisacetylacetone crystallises in enantiomorphous forms of the monoclinic system, with  $a : b : c = 0.8872 : 1 : 1.107$ ;  $\beta = 110^\circ 55'$ . The list of forms observed on a right-handed crystal is

$a(100)$ ,  $c(001)$ ,  $R(\bar{1}01)$ ,  $m(110)$ ,  $m'(\bar{1}\bar{1}0)$ , and  $q(011)$ . The habit is extremely variable. In some crops, the crystals presented the combination of  $m'$  and  $q$  (or  $m$  and  $q'$ ) as shown in Figs. 3 and 2, respectively, but minute traces of  $c$  and  $R$  were always visible with

FIG. 2.

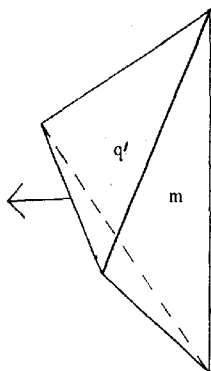
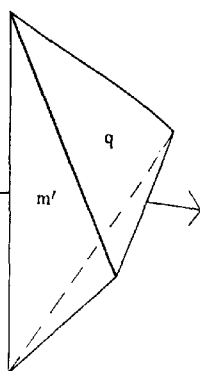


FIG. 3.



a lens. Another frequent habit is that of Figs. 4—5; in another crop, the crystals were greatly elongated along the symmetry axis. Individual crystals were not infrequently distorted to such a degree that they could only be orientated after a preliminary measurement; they could then be uniformly adjusted about the symmetry axis

FIG. 4.

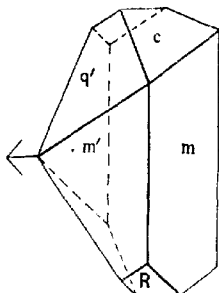
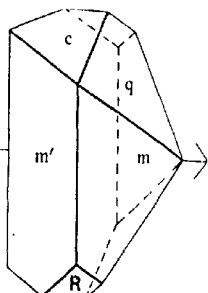


FIG. 5.

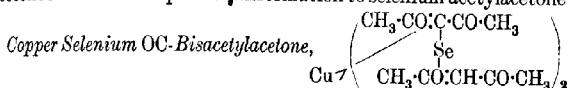


for comparative purposes. Following are the combined results of measurement of four crystals, comprising three of the right-handed types of Figs. 3 and 5 and one of the left-handed variety of Fig. 4.

	$a(100)$ .	$c(001)$ .	$R(\bar{1}01)$ .	$m(110)$ .	$q(011)$ .
$\phi$ .....	$0^\circ 0'$	$*69^\circ 5'$	$*133^\circ 39'$	$0^\circ 0'$	$69^\circ 3'$
$\rho$ .....	90 0	90 0	90 0	*50 21	44 2

In view of the undoubted enantiomorphism, the substance was examined for optical activity. The crystals were segregated into the opposite modifications by the help of the unambiguous *g*-faces, dissolved separately in benzene, and examined in the polarimeter. The concentration of the dissolved dextro-crystals was 4.26 grams per 100 c.c. of solution, that of the laevo-crystals being 3.64 grams. Both solutions were inactive and therefore the enantiomorphism of form cannot be referred to any enantiomorphism of molecular configuration. The constitution ascribed to this substance is in harmony with these experimental results.

*Dissociation of Selenium OC-Bisacetylacetone.*—In concentrated solution in hot alcohol dissociation set in rapidly, the liquid became yellow, and selenium acetylacetone separated. With methyl alcohol, the same change occurred and acetylacetone was detected in the mother-liquors. Selenium bisacetylacetone was also dissociated on warming with water, acetylacetone escaped with the steam, and the residue was pure selenium acetylacetone. The dissociation occurred only incompletely in warm acetonitrile, but not in chloroform, benzene, or light petroleum. A few drops of benzoyl chloride added to an ethereal solution of the bisacetylacetone induced a complete transformation to selenium acetylacetone.



—A chloroform solution of selenium OC-bisacetylacetone was shaken with ammoniacal cupric acetate, the sage-green copper derivative dissolved in the organic liquid to an intense bluish-green solution, from which the product was obtained on evaporation or by precipitation with light petroleum (Found: Se = 25.92, 26.38; Cu = 10.98, 10.81.  $\text{C}_{20}\text{H}_{26}\text{O}_8\text{Se}_2\text{Cu}$  requires Se = 25.72; Cu = 10.32 per cent.).

In boiling chloroform, the salt underwent slow decomposition, and owing to its sparing solubility in pure benzene only very dilute solutions were available for the ebullioscopic determination of molecular weight:  $M = 683, 571$  ( $c = 1.9$ ); the above formula requires  $M = 616$ .

*Selenium C-ethyl-OC-Bisacetylacetone* (Formula II).

C-Ethylacetylacetone was obtained by Combes's method as an oil boiling at 177–180°. To 3.5 grams of this ketone, dissolved in 10 c.c. of alcohol, was added 1 gram of powdered selenium acetylacetone, the mixture was heated under reflux for ten minutes, and the resulting solution evaporated to dryness in a vacuum over sodium hydroxide. The residue, crystallised from light petroleum,

separated in short, rod-like needles or compact prisms. The freshly crystallised substance had a faintly farinaceous odour which disappeared on drying; it softened at 65–67°, and liquefaction was completed by 77° or 82°. This *C*-ethylbisacetylacetone was readily soluble in organic media but insoluble in water (Found: C = 47.19; H = 6.08.  $C_{12}H_{18}O_4Se$  requires C = 47.17; H = 5.94 per cent.).

Selenium *C*-ethyl-*OC*-bisacetylacetone gave an intense red coloration with ferric chloride, differing appreciably from the violet coloration with *C*-ethylacetylacetone itself. The pale blue copper salt was soluble in chloroform or benzene to bluish-green solutions. Warming with water or alcohol dissociated the compound into selenium acetylacetone and *C*-ethylacetylacetone. Benzoyl chloride, added to its ethereal solution, induced the precipitation of selenium acetylacetone.

*Interaction of Selenium Acetylacetone with Alkyl and Aryl Thiols.*

1. *With Methyl Mercaptan.*—A viscid, yellow oil of nauseating odour remained on evaporating to dryness the solution obtained by leaving 1 gram of selenium acetylacetone in contact with 0.35 gram of methyl mercaptan in dry ether. The oily product, which could not be induced to solidify, developed an intense red coloration with aquo-alcoholic ferric chloride, and gave a yellowish-green copper salt (0.9 gram) with aqueous cupric acetate. This copper salt was very soluble in cold chloroform and crystallised from benzene in small, green crystals decomposing at 164–167°. These results pointed to the formation of an enolic mixed selenothio-ether,  $CH_3 \cdot C(OH) \cdot C(CO \cdot CH_3) \cdot Se \cdot S \cdot CH_3$ , as the main product, although the reaction was not quantitative. The interaction with other alkyl mercaptans is being studied.

2. *With Thio- $\alpha$ -naphthol.*—Preliminary experiments having shown that with molecular proportions of the reagents a considerable proportion of  $\alpha\alpha$ -dinaphthyl disulphide was produced, the interaction was carried out with excess of selenium acetylacetone, 2.0 grams of which were added to 15 c.c. of dry ether containing 1.5 grams of thio- $\alpha$ -naphthol. After one day at the ordinary temperature, the yellow solution was decanted from undissolved selenium acetylacetone (0.35 gram) and slowly evaporated. A crop of  $\alpha$ -naphthylthioselenium acetylacetone (1.3 grams) separated in large, transparent, yellow crystals. A second crop (1.0 gram) consisted of a mixture of this compound with diselenium bisacetylacetone and  $\alpha\alpha$ -dinaphthyl disulphide. The components of this mixture were separated by dissolving the product in ether, the ethereal solution being shaken with aqueous cupric acetate. The filtrate (a) from the

copper salts (*b*) was allowed to evaporate;  $\alpha\alpha$ -dinaphthyl disulphide separated and was purified by solution in alcohol, when pale yellow crystals were obtained melting at  $89-91^\circ$  (Schertel, *J. pr. Chem.*, 1893, [ii], **47**, 197, gives m. p.  $91^\circ$ ).

The mixed copper salts (*b*) were shaken with ether and dilute sulphuric acid, the yellow ethereal extract evaporated, and the crystalline residue dissolved in light petroleum. On evaporation, this solution yielded large, bright orange crystals and smaller, pale yellow, prismatic crystals; these substances were separated by hand and crystallised separately from petroleum. The orange substance yielded the characteristic prisms of diselenium bisacetylacetone (0.1 gram). The pale yellow material furnished more  $\alpha$ -naphthylthioselenium acetylacetone, the total yield being 63 per cent. of the calculated amount.

$\alpha$ -Naphthylthioselenium acetylacetone (Formula X) separated from ether or light petroleum in bright cowslip-yellow crystals readily soluble in organic solvents. It was decidedly enolic, giving a greenish-yellow copper salt and a red ferric chloride coloration. After preliminary softening, it melted at  $81-83^\circ$  to a transparent, yellow liquid (Found: C = 53.28; H = 4.29; S = 9.14; Se = 22.89.  $C_{15}H_{14}O_2SSe$  requires C = 53.36; H = 4.18; S = 9.50; Se = 23.47 per cent.).

3. With Thio- $\beta$ -naphthol.—Selenium acetylacetone (0.5 gram) dissolved slowly but completely in 7 c.c. of dry ether containing 0.6 gram of thio- $\beta$ -naphthol to an orange-yellow solution, which on concentration yielded nodular crystals of  $\beta\beta$ -dinaphthyl disulphide, separating from benzene or light petroleum in pale yellow, silvery flakes melting at  $139-141^\circ$  (Cleve, *Ber.*, 1888, **21**, 1100, gives m. p.  $139^\circ$ ; compare *Ber.*, 1896, **29**, 1327). The yellow, ethereal filtrate from this disulphide contained enolic substances as in the foregoing reaction with thio- $\alpha$ -naphthol, with the difference that the proportion of disulphide was greater. This and other condensations with aromatic thiols are under examination.

## II. Selenium Benzoylacetone and cyclo-Tri-selenium Bisbenzoylacetone.

1. Selenium tetrachloride (4.6 grams) was suspended in 50 c.c. of dry ether and added to 6.8 grams of benzoylacetone dissolved in 60 c.c. of the same solvent. After three hours, a pale red solution was obtained which on evaporation in a current of air evolved hydrogen chloride and left a greenish-yellow oil. This residue, triturated with successive small portions of alcohol, furnished an almost white powder (0.7 gram). The filtrates slowly yielded further crops of this product (1.4 grams), which on extraction in a



Soxhlet apparatus with benzene gave masses of small, pale yellow needles of *selenium benzoylacetone*, decomposing at  $200^{\circ}$ . The benzene mother-liquors contained *cyclotriselenium bisbenzoylacetone*, which was identified more precisely in the following preparation.

2. To 20.5 grams of selenium tetrachloride (1 mol.), suspended in 160 c.c. of anhydrous chloroform B.P., were added with shaking during fifteen minutes at the ordinary temperature 41 grams of dry copper benzoylacetone ( $1\frac{1}{2}$  mols.) A rise of temperature was noticed, the selenium tetrachloride disappeared, and after one hour the precipitated cupric chloride, containing a red seleniferous tar, was removed. The red chloroform filtrate, evaporated at the ordinary temperature in a stream of air, left an oily residue, which was separated by means of alcohol into a less soluble product (a) and more soluble *chlorobenzoylacetone* (b) contaminated with ill-defined seleniferous products.

The product *a* was extracted repeatedly with small portions of cold chloroform B.P., and the residue, consisting of selenium benzoylacetone (2.5 grams), purified by crystallisation from toluene.

The chloroform filtrates on evaporation yielded orange *cyclotriselenium bisbenzoylacetone*, which after washing with cold dry ethyl acetate consisted of small, orange-yellow crystals (3.1 grams) purified by crystallisation from hot anhydrous ethyl acetate or by precipitation from chloroform by alcohol or from benzene or toluene by light petroleum.

*cyclotriselenium bisbenzoylacetone* (formula XVIII), when thus separated from selenium benzoylacetone, was obtained in small, prismatic, bright yellow crystals often showing rhombic cross sections; it was inodorous, insoluble in alcohol, ether, or water, but dissolving more freely in cold benzene or chloroform. It crystallised best from boiling ethyl acetate, in which it is five times as soluble as is selenium benzoylacetone. The solutions of this triselenium compound in organic media had a bright yellow colour, differing also in this respect from the very pale yellow solutions of selenium benzoylacetone. *cyclotriselenium bisbenzoylacetone* sintered and darkened at  $190-195^{\circ}$ , liberating selenium and changing to a dark tar at  $196-200^{\circ}$  [Found: C = 43.20; H = 3.14; Se = 42.26; by ebullioscopic method in benzene ( $c = 1.81$ ),  $M = 582$ .  $C_{20}H_{16}O_4Se_3$  requires C = 43.04; H = 2.89; Se = 42.59 per cent.;  $M = 558$ ]. This triselenium compound was decomposed readily by hot concentrated hydrochloric acid; it was insoluble in cold 5*N*-sodium hydroxide, but subsequently decomposed by this reagent into acetophenone and selenium; it had no enolic properties, giving neither ferric coloration nor copper salt. It remained unchanged in cold aqueous potassium hydroxide.

sulphite. Hydriodic acid reacted with the triselenium compound, yielding iodine, red selenium, and *diselenium bisbenzoylacetone* (see p. 2458).

The crystals of *cyclotriselenium bisbenzoylacetone* are too poorly developed to yield accurate results, but a fragmentary optical examination points to the monoclinic system. No crystallographic resemblance was in any case to be expected with the chemically analogous trithiobis-acetylacetone of Angeli and Magnani (*Gazzetta*, 1894, 24, [1], 342), which Negri found to be orthorhombic—in view of the highly sensitive relation of crystalline form to change of chemical composition.

*Selenium benzoylacetone* (formula XV) separated from toluene in small, pale primrose-yellow, six-sided plates having, when freshly crystallised, a faint odour of elderberries. It was insoluble in water, ether, or alcohol, dissolved only sparingly in boiling chloroform, benzene, or ethyl acetate, and was rather more soluble in toluene or glacial acetic acid [Found: C = 49.94; H = 3.61; Se = 32.67; *M*, by ebullioscopic method in toluene ( $c = 0.719$ ,  $k = 33.8$ ), = 456, 422.  $(C_{10}H_8O_2Se)_2$  requires C = 50.16; H = 3.37; Se = 33.09 per cent.; *M* = 478].

Selenium benzoylacetone exists in two closely related varieties, one becoming discoloured at 175° and decomposing to a reddish-brown tar at 200°, the other not changing in colour below 207°, but melting rather sharply at 210–212°. Selenium benzoylacetone was also obtained from silver benzoylacetone with selenium tetrachloride in chloroform solution, and in this preparation the formation of *cyclotriselenium bisbenzoylacetone* was not noticed. Selenium benzoylacetone had no enolic properties, was insoluble in caustic alkalis, and inactive towards ferric and cupric compounds. When left in contact with cold 5*N*-sodium hydroxide, it was decomposed, yielding acetophenone and red selenium, but it remained unchanged or several hours in cold aqueous potassium metabisulphite. Aniline and phenylhydrazine decomposed the substance with elimination of selenium.

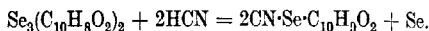
Selenium benzoylacetone crystallises in elongated, six-sided plates with a dome termination of 64°. The extinction is straight and a positive bisectrix emerges normal to the plate: whether acute or obtuse could not be determined with certainty. In any case, the optic axial plane contains the morphological direction of elongation.

#### *Cyano-3-selenium Benzoylacetone* (Formula XIX).

When added to 8 c.c. of anhydrous hydrogen cyanide in 10 c.c. of dry ether, 2.42 grams of selenium benzoylacetone dissolved in

two hours at the ordinary temperature. The solution, evaporated under reduced pressure, left a glue—probably an unstable cyanohydrin—which then slowly evolved hydrogen cyanide and solidified to a mass of colourless, brittle crystals having an odour of burnt rubber (yield quantitative). When recrystallised from light petroleum (b. p. 40–100°), it separated in transparent needles softening at 68°, melting at 70° to a colourless liquid which reddened at 110° [Found: Se = 29.05; N = 5.33; *M*, cryoscopically in benzene (*c* = 0.901), = 250.  $C_{11}H_9O_2NSe$  requires Se = 29.74; N = 5.26 per cent., and *M* = 266].

*Cyano-3-selenium benzoylacetone* was also obtained quantitatively from cyclotriselenium bisbenzoylacetone (pp. 2439, 2454). The finely powdered triselenium compound (0.655 gram) was left at 0° for eighteen hours in 3 c.c. of hydrogen cyanide and 3 c.c. of dry ether. Red selenium separated and became transformed even at this low temperature to the black variety (94 per cent.). The mixture was evaporated to dryness, and the residue dissolved in benzene, filtered from selenium, and concentrated to obtain the cyano-derivative (quantitative yield). The reaction takes place as follows:



The cyano-compound was readily soluble in benzene or chloroform, less soluble in carbon tetrachloride, and crystallised from these solvents on adding light petroleum; it dissolved in alcohol, but with slow decomposition. With cupric acetate, it at once gave the greenish-blue *copper* salt (m. p. 131°); with ferric chloride in aquo-alcoholic chloroform, enolisation set in after a few seconds, the liquid assuming an intense red shade. The cyano-compound was very sensitive to sunlight, selenium being eliminated.

*3-Chlorobenzoylacetone*,  $C_6H_5 \cdot CO \cdot CCl(OH) \cdot CH_3$  (product *b*, p. 2454).—The alcoholic mother-liquors from which selenium benzoylacetone and cyclotriselenium bisbenzoylacetone had separated were allowed to evaporate in air until a lachrymatory oil remained, which was freed from selenium by extraction with cold light petroleum. This extract was shaken with copper acetate in presence of chloroform, added to remove copper benzoylacetone.

The light green *copper chlorobenzoylacetone* was collected, dried (16 grams), and decomposed by dilute sulphuric acid in presence of ether to take up the chlorobenzoylacetone. The ethereal layer was rapidly evaporated in a current of air and the residual solid quickly spread on porous tile, otherwise the product became liquid and was not rendered solid except by repeating the treatment with the copper salt.

Chlorobenzoylacetone was extremely soluble in organic solvents

and very difficult to crystallise; it formed colourless needles melting indefinitely at 40–43° (Found: Cl = 17.65.  $C_{10}H_9O_2Cl$  requires Cl = 18.04 per cent.). This chlorinated  $\beta$ -diketone had a pungent lachrymatory odour and a considerable vapour pressure at the ordinary temperature. It was markedly enolic, giving a red, ferric coloration and the green copper salt. With *p*-nitrophenylhydrazine, it yielded a crystalline product.

4.*Chloro-5(or 3)-phenyl-1-p-nitrophenyl-3(or 5)-methylpyrazole.*—Chlorobenzoylacetone (0.8 gram) was heated under reflux in 20 c.c. of absolute alcohol for one hour with an equal weight of *p*-nitrophenylhydrazine and the solution concentrated to the crystallising point, when 1.1 grams of reddish-orange crystals were obtained. Successive crystallisation from alcohol and glacial acetic acid removed a red by-product and furnished the pyrazole in pale orange needles or elongated plates melting at 156–158° (Found: N = 13.76; Cl = 11.46.  $C_{16}H_{13}O_2N_3Cl$  requires N = 13.40; Cl = 11.31 per cent.). The homogeneity of the foregoing pyrazole suggests that chlorobenzoylacetone enolises only in one direction.

*Preparation of Halogenated  $\beta$ -Diketones from Copper Derivatives of the Diketones.*

Dry copper benzoylacetone was dissolved in chloroform and the ice-cold solution treated with dry chlorine until the precipitation of cupric chloride was complete. The filtrate, when evaporated, yielded an oil which on extraction with ether and treatment with ammoniacal copper acetate gave the copper derivative of chlorobenzoylacetone, from which the chloro-derivative was liberated by dilute mineral acid; crystallised from light petroleum, this specimen of chlorobenzoylacetone melted at 42–44° and was identical with that from the selenium tetrachloride reaction.

Copper acetylacetone, when similarly chlorinated, gave a chloroacetylacetone identical with that obtained from selenium tetrachloride and acetylacetone. This method of halogenation through the copper derivatives of the  $\beta$ -diketones is in all probability capable of considerable extension.

*Diselenium Bisbenzoylacetone (Formula XVI).*

1. *Preparation from Selenium Benzoylacetone.*—One gram of powdered selenium benzoylacetone was shaken for ten minutes with 1 c.c. of 50 per cent. hydriodic acid, 100 c.c. of ether, and 30 grams of ice with gradual addition of 40 c.c. of *N*/10-sodium thiosulphate to remove the liberated iodine. The ethereal layer on evaporation yielded orange crystals of *diselenium bisbenzoylacetone* (0.6 gram), about 0.2 gram of selenium benzoylacetone being recovered un-

changed. Another experiment with 1.7 grams of selenium benzoylacetone gave 0.6 gram of unchanged material and 0.9 gram of diselenium bisbenzoylacetone. By using comparatively dilute hydriodic acid, very little benzoylacetone was produced.

2. *Preparation from cycloTriselenium Bisbenzoylacetone.*—0.5 Gram of the triselenium compound, when shaken at 0° with 0.5 c.c. of 50 per cent. hydriodic acid (decolorised), 50 c.c. of ether, and 10 grams of ice, gave selenium and iodine simultaneously, the latter being removed by *N*/10-thiosulphate, added gradually. The ethereal layer, filtered from red selenium and a little unchanged triselenium compound, yielded 0.2 gram of diselenium bisbenzoylacetone. The product from either of the foregoing preparations closely resembled diselenium bisacetylacetone and crystallised in bright orange, six-sided prisms; it was quite insoluble in water

and nearly so in alcohol, but dissolved readily in ether, chloroform, or cold benzene and more sparingly in boiling light petroleum, from which solvent it crystallised most readily; it softened at 65° and became liquid from 80–90° [Found: C = 49.88; H = 3.88; Se = 32.84; *M*, by cryoscopic method in benzene (*c* = 1.34), = 448.  $C_{20}H_{18}O_4Se_2$  requires C = 49.95; H = 3.77; Se = 32.96 per cent.; *M* = 480].

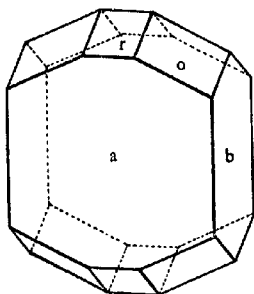
Diselenium bisbenzoylacetone dissolved somewhat sparingly in cold

5*N*-sodium hydroxide and rapidly decomposed, with elimination of selenium and production of acetophenone. Etheral alcoholic ferric chloride developed a violet-red coloration; aqueous cupric acetate furnished a brownish-yellow *copper* derivative, insoluble in water but dissolving sparingly in chloroform. With alcoholic phenylhydrazine, the diselenium compound reacted even in the cold; an intermediate salmon-pink compound was formed which speedily generated red selenium, especially on warming.

*Diselenium Bisbenzoylacetone and its Isomorphism with Dithiobisbenzoylacetone.*

The orange crystals of diselenium bisbenzoylacetone prove to be isomorphous with the corresponding dithio-compound (see below). The system is orthorhombic with  $a : b : c = 0.7341 : 1 : 0.4110$ , the forms developed being  $b(010)$ ,  $a(100)$ ,  $o(111)$ , and  $r(101)$ , as illustrated by Fig. 6. Following are the results of measurement of two crystals.

FIG. 6.



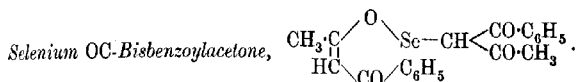
	<i>b</i> (010).	<i>a</i> (100).	<i>o</i> (111).	<i>r</i> (101).
$\phi$ .....	0° 0'	89° 58'	*53° 43'	90° 32'
$\rho$ .....	90 0	90 0	*34 47	29 14

Optically the crystals exhibit a strong dichroism when resting on *b* (010), but not on *a* (100), the transmitted colours being deep orange for *a*-axis vibrations, and lemon-yellow for the *b*- and *c*-axes. The optic axial plane is *c* (001), but it was not possible to determine the several orientations of the two bisectrices.

The dithio-analogue, prepared by the method of Vaillant (*Bull. Soc. chim.*, 1898, [iii], 19, 833), is only distinguishable from the diselenium compound by some form of measurement. The habit and forms are those of Fig. 6, the axial ratios being *a* : *b* : *c* = 0.6929 : 1 : 0.3966. The close similarity of angles will be evident from a comparison of the preceding and the following tables.

	<i>b</i> (010).	<i>a</i> (100).	<i>o</i> (111).	<i>r</i> (101).
$\phi$ .....	0° 0'	90° 0'	*55° 17'	90° 18'
$\rho$ .....	90 0	90 0	*34 51	29 48

A good cleavage was observed parallel to *b* (010), through which emerges a positive acute bisectrix. The optic axial plane is *c* (001) and the angle quite wide.



One gram of powdered selenium benzoylacetone, suspended in a solution of 3 grams of benzoylacetone in 20 c.c. of chloroform B.P., did not dissolve even after heating under reflux for five minutes, but on adding a speck of solid sodium hydroxide the selenium compound dissolved completely to a transparent, pale yellow solution. After warming for ten minutes, the chloroform was evaporated under reduced pressure, when the residual oil solidified and was extracted with cold light petroleum to remove excess of benzoylacetone. The residue (0.5 gram) crystallised from benzene and light petroleum in minute, white, inodorous prisms sintering at 100°, melting to a transparent liquid at 134–136°, and decomposing at higher temperatures [Found: C = 59.72; H = 4.85; *M*, by the ebullioscopic method in benzene (*c* = 1.583), = 437. C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>Se requires C = 59.83; H = 4.52 per cent.; *M* = 401].

Selenium bisbenzoylacetone was only obtained in favourable yield when an excess of benzoylacetone was employed; an optimum result (0.55 gram) was obtained by adding a trace of sodium hydroxide to 0.55 gram of selenium benzoylacetone, 1.5 grams of benzoylacetone, and 10 c.c. of chloroform B.P. after boiling for three

minutes. This bis-compound was insoluble in water or light petroleum, sparingly soluble in ether, alcohol, or cold benzene, dissolving more readily in the hot solvent or in chloroform. It had no acidic properties, was insoluble in cold 5*N*-sodium hydroxide, although decomposing in contact with this reagent. It did not yield a copper derivative, and with ferric chloride in alcoholic chloroform solution the red coloration only developed slowly. On boiling with alcohol or any moist solvent, selenium bisbenzoylacetone reverted to selenium benzoylacetone and benzoylacetone, but the bis-compound crystallised unchanged from its solution in boiling benzene.

1. *Transformation of Selenium Benzoylacetone into Selenium Acetylacetone*.—Powdered selenium benzoylacetone (1 gram) remained undissolved in 8.5 grams of acetylacetone and 10 c.c. of pure ethyl alcohol even on refluxing, but the addition of a speck of solid sodium hydroxide induced complete solution to a pale yellow liquid, from which, after evaporating off the solvent, a yellow glue was obtained. Extraction with cold light petroleum removed benzoylacetone; the cold alcoholic solution of the residue from the petroleum extraction deposited pale yellow selenium acetylacetone mixed with a smaller proportion of selenium benzoylacetone.

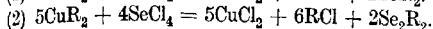
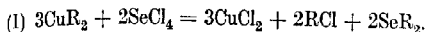
2. *Transformation of Selenium Acetylacetone into Selenium Benzoylacetone*.—Selenium acetylacetone (1 gram) dissolved in a warm solution of 2.5 grams of benzoylacetone and 10 c.c. of chloroform B.P., but only after adding a trace of sodium hydroxide. After removing the solvent, the glutinous residue, which contained unchanged benzoylacetone and selenium bisacetylacetone, was crystallised repeatedly from benzene and light petroleum in order to separate selenium bisbenzoylacetone. This intermediate product was then converted into selenium benzoylacetone by boiling with alcohol.

### III. *Action of Selenium Tetrachloride on C-Ethylacetylacetone and on its Copper Derivative.*

Several attempts were made to introduce selenium into the molecule of *C*-ethylacetylacetone by bringing together the tetrachloride and the alkyl  $\beta$ -diketone in ethereal solution, but under these conditions the former acted as a chlorinating agent and the only recognisable products were selenium and 3-chloro-3-ethylacetylacetone.

*C*-Ethylacetylacetone prepared by the action of ethyl iodide on sodium acetylacetone (Combes, *Ann. Chim. Phys.*, 1887, [vi], 12, 247), obtained as a fragrant, pale yellow oil boiling at 177–180°,

was converted into its light blue copper derivative by treatment with copper acetate and sufficient ammonia or sodium hydroxide to neutralise the liberated acetic acid. This copper salt reacted with selenium tetrachloride in the presence of dry chloroform, and two organic selenium derivatives were obtained in accordance with the following equations, where R is the univalent radicle of the diketone.



Employing four molecular proportions of copper *C*-ethylacetylacetone to three of selenium tetrachloride, an optimum total yield of the two products was obtained by adding rapidly 11.7 grams of dry copper *C*-ethylacetylacetone to 6.2 grams of selenium tetrachloride suspended in 50 c.c. of dehydrated chloroform B.P. at 0°. After the mixture had been shaken at the ordinary temperature for one hour, the colour changed from intense greenish-black to greenish-brown and cupric chloride was precipitated. This chloride, when dissolved in water, left a small amount of red powder rapidly becoming jet black, which contained both copper and selenium but no organic material.

The golden-yellow syrup left on evaporating the chloroform filtrate was dissolved in ethyl alcohol and the solution concentrated at the ordinary temperature, when 1.3 grams of *selenium bis-C-ethylacetylacetone* (XX) separated. The mother-liquor, stirred with more alcohol and left to evaporate, yielded 0.9 gram of yellow *diselenium bis-C-ethylacetylacetone* (XXI). Subsequent crops (1.8 grams) consisted of mixtures of these two compounds. This mixture was redissolved in alcohol and the solution allowed to crystallise very slowly, so that large, prismatic crystals of the two compounds were obtained. The separation was in favourable cases effected by hand picking. The total yield of separated compounds was 60 per cent. of the calculated amount, the product consisting of equal proportions of the two compounds.

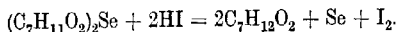
*Selenium bis-C-ethylacetylacetone* (formula XX) became the sole product on adding 2.2 grams of dry copper *C*-ethylacetylacetone (2 mols.) to 0.77 gram of selenium tetrachloride (1 mol.) in 20 c.c. of chloroform B.P. The pale green filtrate from the precipitated cupric chloride was shaken with ether and dilute sulphuric acid, and the ethereal extract evaporated until 0.6 gram of the compound was obtained (yield 50 per cent.). *Selenium bis-C-ethylacetylacetone*, crystallising from alcohol in colourless, transparent, six-sided prisms or needles, was sparingly soluble in boiling water, from which it separated on cooling. It dissolved sparingly in light petroleum and more readily in ether, benzene, or chloroform. The crystals



melted at 81–82° to a transparent, colourless liquid which did not liberate selenium until about 200° [Found: C = 50·41; H = 6·81; Se = 23·36; *M*, by cryoscopic method in benzene (*c* = 1·95) = 296.  $C_{14}H_{22}O_4Se$  requires C = 50·40; H = 6·65; Se = 23·75 per cent.; *M* = 333].

Selenium bis-*C*-ethylacetylacetone was non-enolic and gave no coloration with aquo-alcoholic ferric chloride even on boiling; it was insoluble in cold 5*N*-sodium hydroxide, but slowly decomposed in this reagent with reddening, evolving an odour of methyl propyl ketone. With warm concentrated hydrochloric acid, the compound was decomposed liberating selenium; it did not combine additively with bromine in chloroform solution, but was slowly decomposed by this halogen. It gave no reaction with aqueous potassium hydrogen sulphite, even on warming.

The constitution of selenium *C*-ethylacetylacetone is confirmed by its quantitative decomposition with 50 per cent. hydriodic acid in presence of ether into *C*-ethylacetylacetone and selenium, the iodine set free being titrated:



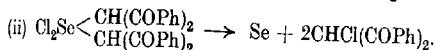
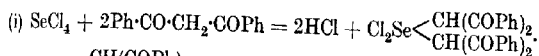
*Diselenium bis-C-ethylacetylacetone* (formula XXI), the less fusible and less soluble substance obtained by the interaction of selenium tetrachloride and copper *C*-ethylacetylacetone, became the sole product when the reagents were taken, respectively, in the proportions of 4 to 5 molecules: 7·8 grams of copper derivative were added all at once to 4·3 grams of tetrachloride in 40 c.c. of dried chloroform B.P. at 0°. After one hour, the filtrate from cupric chloride left on concentration an orange-coloured oil which, after mixing with alcohol, yielded on further evaporation 1·2 grams of the pure substance.

*Diselenium bis-C-ethylacetylacetone* crystallised from alcohol in lemon-yellow, six-sided needles or prisms; it melted at 117–118°, after softening at 116°, to a transparent, yellow liquid which reddened and rapidly decomposed at 210°. The compound was sparingly soluble in light petroleum, dissolving more freely in ether, benzene, or chloroform; it was non-enolic, giving no coloration even on warming with aquo-alcoholic ferric chloride, and was insoluble in 5*N*-sodium hydroxide, but decomposed when left in this reagent, giving selenium and methyl propyl ketone. Decomposition also occurred with bromine in chloroform. With potassium hydrogen sulphite (2 to 4 molecules), it yielded *C*-ethylacetylacetone, selenium, and probably potassium selenodithionate. When the sulphite was in large excess no selenium was set free, the element dissolving probably to form potassium selenosulphate.

Diselenium bis-*C*-ethylacetylacetone was decomposed quantitatively by hydriodic acid in presence of ether into *C*-ethylacetylacetone and red selenium: 0.300 gram of the substance gave 90 per cent. of the calculated amount of free iodine as titrated by thiosulphate [Found: C = 40.49, 40.94; H = 5.35, 5.50; Se = 37.85; *M*, by cryoscopic method in benzene (*c* = 1.17), = 366. (C<sub>7</sub>H<sub>11</sub>O<sub>2</sub>Se)<sub>2</sub> requires C = 40.73; H = 5.38; Se = 38.39 per cent.; *M* = 412].

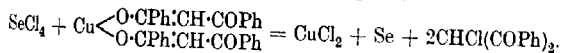
IV. *Action of Selenium Tetrachloride on Dibenzoylmethane and on its Copper Derivative.*

Several attempts were made to introduce selenium into the molecule of dibenzoylmethane by the interaction of the tetrachloride and this aromatic β-diketone. In molecular proportions, the two reagents, employed in presence of dry ether, gave hydrogen chloride, red selenium, and *chlorodibenzoylmethane*, the tetrachloride acting mainly as a chlorinating agent. With two molecular proportions of dibenzoylmethane, the yield of its chloro-derivative was almost quantitative, the amount of unchanged diketone being very small. The reaction appeared to take the following course:



The intermediate compound was very unstable, either decomposing as in equation (ii) or by slow access of moisture yielding a small proportion of an amorphous, pink powder which melted at 150—160° and no longer contained chlorine.

*Chlorodibenzoylmethane*, C<sub>6</sub>H<sub>5</sub>·CO·CHCl·CO·C<sub>6</sub>H<sub>5</sub>, was prepared as in the foregoing experiments and also by the interaction of molecular proportions of selenium tetrachloride and copper dibenzoylmethane in dry chloroform B.P. (2 parts):



The weights of products are in substantial agreement with the foregoing equation.

When this reaction was carried out at 0°, the chlorination process was partly replaced by one in which selenium was introduced, and a small amount of *selenium bisdibenzoylmethane* was obtained.

*Chlorodibenzoylmethane* crystallised from methyl alcohol in colourless needles having a peculiar mixed aromatic lachrymatory odour. It had a considerable vapour pressure at the ordinary

temperature and melted without decomposition at 87—88° (Found: Cl = 13.55.  $C_{15}H_{11}O_2Cl$  requires Cl = 13.71 per cent.).

Chlorodibenzoylmethane was not markedly enolic, giving neither coloration with aquo-alcoholic ferric chloride nor copper derivative with ammoniacal copper acetate. It dissolved only slowly and sparingly in 5*N*-sodium hydroxide, hydrolysis occurring on warming with production of an odour resembling that of acetophenone. In these properties the chloro-derivative resembles bromodibenzoylmethane (m. p. 93°), which is described as being non-enolic (*Ber.*, 1890, 23, 3377; *Annalen*, 1899, 308, 247).

*Selenium Bisdibenzoylmethane* (Formula XXIII).

The yellowish-green copper salt of dibenzoylmethane, precipitated quantitatively on shaking aqueous copper acetate with an ethereal solution of the diketone, was dried at 100° for use in the following experiments.

(i) 3 Mols. of  $SeCl_4$  : 4 mols. of copper salt.—To 2.0 grams of selenium tetrachloride, suspended in 20 c.c. of dehydrated chloroform B.P. cooled to 0°, were added quickly 6.2 grams of dry copper dibenzoylmethane and 10 c.c. of chloroform. After one and a half hours, cupric chloride and a trace of red selenium were removed and the filtrate evaporated to a reddish-yellow paste, which was extracted with warm alcohol to remove dibenzoylmethane and its chloro-derivative. The red crystalline residue was recrystallised from ethyl acetate, when pale yellowish-white prisms of *selenium bisdibenzoylmethane* separated.

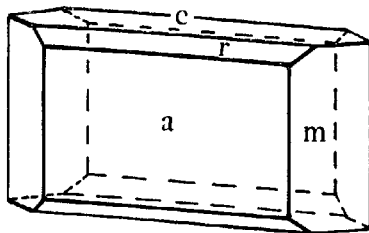
(ii) 4 Mols. of  $SeCl_4$  : 5 mols. of copper salt.—Copper dibenzoylmethane (16.7 grams) and 5.7 grams of selenium tetrachloride were mixed in 75 c.c. of chloroform at 0° and after three and a half hours the filtrate from the precipitated cupric chloride was evaporated to remove solvent and the golden-yellow, syrupy residue seeded with selenium bisdibenzoylmethane, left over-night, and the mixture of crystals and oil washed successively with cold alcohol (a) and ethyl acetate (b). The pale yellow, crystalline residue (2.7 grams) consisted of pure selenium bisdibenzoylmethane. The ethyl acetate extract (b) was evaporated, the residual syrup washed successively with cold alcohol (a) and ethyl acetate. The insoluble residue, consisting of selenium dibenzoylmethane, a bright yellow powder (0.4 gram), was now insoluble in boiling ethyl acetate (distinction from selenium bisdibenzoylmethane). This product was subsequently obtained in larger amount and examined more completely (p. 2466). The alcoholic extracts (a) from the foregoing separation contained a considerable amount of chlorodibenzoylmethane mixed

with dibenzoylmethane: the latter was removed in the form of its copper salt.

Selenium bisdibenzoylmethane crystallised from dry ethyl acetate in large, yellowish-white, six-sided prisms softening at  $143^\circ$  and melting at  $150$ – $152^\circ$  to a transparent, yellow liquid (Found: C = 68.46; H = 4.37; Se = 15.02.  $C_{30}H_{22}O_4Se$  requires C = 68.53; H = 4.22; Se = 15.07 per cent.).

As proved by optical examination, the pseudo-orthorhombic crystals of selenium bisdibenzoylmethane are really monoclinic, but the imperfect nature of the reflections (due to curvature) do not permit a rigid geometrical proof. The elements, as obtained by a mutual adjustment of the poles of a gnomonic projection, are  $a:b:c = 1.07:1:0.75$ ,  $\beta = 91\frac{1}{2}^\circ$ . The list of forms is  $a(100)$ ,  $m(110)$ ,  $c(001)$ ,  $r(101)$ , and  $R(\bar{1}01)$ , the relative development being

Fig. 7.



that of Fig. 7. Following are the approximate angular values obtained from two crystals.

	$m(110)$ .	$a(100)$ .	$c(001)$ .	$r(101)$ .	$R(\bar{1}01)$ .
$\phi$ .....	$43^\circ$	$90^\circ$	ca. $90^\circ$	$90^\circ$	$90^\circ$
$\rho$ .....	90	90	1	37	35

There is an imperfect cleavage parallel to  $a(100)$ , through which an optic axis emerges very obliquely. Another optic axis is visible through  $c(001)$ , so that the axial plane is  $b$ . A  $35^\circ$  extinction on  $m$  (with the vertical edge) is another proof that the system is not orthorhombic.

From dry benzene this selenium derivative crystallised in aggregates of minute, white needles containing one molecular proportion of the solvent (Found:  $C_6H_6 = 12.48$ .  $C_{30}H_{22}O_4Se \cdot C_6H_6$  requires  $C_6H_6 = 12.94$  per cent.). In spite of the combination with benzene, a molecular-weight determination by the ebullioscopic method in this solvent ( $k = 25.7$ ) gave satisfactory results for the solvent-free substance:  $c = 1.755$ ,  $M = 496$ ;  $c = 2.537$ ,  $M = 498$ .  $C_{30}H_{22}O_4Se$  requires  $M = 525.5$ . This solvent of crystallisation is

removed at 100°, the needles crumbling into white, skeletal forms softening at 143° and melting to a yellow liquid at 150–152°. The compound dissolved sparingly in alcohol and more freely in benzene or chloroform; insoluble in cold 5*N*-sodium hydroxide, it was decomposed on boiling with elimination of selenium, an odour of acetophenone becoming appreciable. This selenium derivative was comparatively inert and stable; it was not affected by cold potassium hydrogen sulphite and only very slowly on warming; it gave no copper salt, and its chloroform solution mixed with aqueous alcoholic ferric chloride gave at first no coloration, but in a few seconds a red colour developed, the liquid becoming cloudy owing to formation of a dark precipitate.

Selenium bisdibenzoylmethane was decomposed by warm concentrated hydrochloric acid, a small proportion of selenium separated, and this elimination was completed by the addition of sodium sulphite. Dilute hydriodic acid decomposed this selenium compound (0.4 gram) quantitatively, giving red selenium, dibenzoylmethane, and free iodine equivalent to 13.7 c.c. of *N*/10-thiosulphate (calc., 15.2 c.c.).

In connexion with the formation of selenium bisdibenzoylmethane, it is of interest to show how dependent the preparation is on the proportion of the two reagents. Molecular proportions of selenium tetrachloride and copper dibenzoylmethane led to viscid products, from which only a small amount of selenium dibenzoylmethane could be extracted. The optimum yield (42 per cent.) of selenium bisdibenzoylmethane was obtained by using 5.5 grams of selenium tetrachloride (2 mols.) and 19.0 grams of copper dibenzoylmethane (3 mols.) in 65 c.c. of dry chloroform B.P. at 0°. The filtrate from copper chloride, evaporated to a syrupy consistence, was covered with alcohol and seeded with crystals of the selenium compound, when the solution solidified. The alcoholic ethyl acetate washings of the crystalline precipitate contained chlorodibenzoylmethane, the reaction having proceeded in accordance with equation *a* (p. 2441).

*Selenium Dibenzoylmethane (Formula XXV).*

The optimum yield of selenium dibenzoylmethane was obtained as follows. To a cooled solution of 9.9 grams of selenium tetrachloride in 150 c.c. of chloroform B.P. were added quickly 28.5 grams of copper dibenzoylmethane, and the mixture was shaken at intervals for two and a half hours at the laboratory temperature. The filtrate from copper chloride was evaporated until free from chloroform, the residual syrup stirred, left for twelve hours, and extracted repeatedly with cold alcohol. The remaining solid was extracted

with cold ethyl acetate (*a*). The final residue—a primrose-yellow powder—contained the whole of the selenium bisdibenzoylmethane and selenium dibenzoylmethane isolated in this experiment; the two products were separated by making use of the comparative insolubility of the latter in boiling ethyl acetate. The yield of the bis-compound was 5 grams, that of the selenium dibenzoylmethane (m. p. 211°) was 1.4 grams or 10 per cent. calculated on the selenium tetrachloride.

Selenium dibenzoylmethane crystallised from benzene in lustrous, pale golden-yellow plates containing 2 molecules of benzene of crystallisation (Found: in air-dried specimens heated at 100°,  $C_6H_6 = 20.57$ .  $C_{30}H_{20}O_4Se_2 \cdot 2C_6H_6$  requires  $C_6H_6 = 20.58$  per cent. Found: in benzene-free substance,  $C = 59.10$ ,  $59.79$ ;  $H = 3.40$ ,  $3.49$ ;  $Se = 25.63$ ;  $M$ , in boiling benzene, = 583.  $C_{30}H_{20}O_4Se_2$  requires  $C = 59.75$ ;  $H = 3.35$ ;  $Se = 26.28$  per cent.;  $M = 602$ ). Selenium dibenzoylmethane was very sparingly soluble in boiling ethyl acetate and moderately soluble in benzene, dissolving readily in chloroform; it yielded yellow solutions and when freed from benzene was obtained as a pale primrose-yellow powder melting sharply at 211° to a deep yellow liquid liberating selenium. The substance was not enolic and was insoluble in cold 5*N*-sodium hydroxide, but decomposed on warming. It was stable to 15 per cent. hydrochloric acid and dissolved in concentrated sulphuric acid to an intensely scarlet solution, the colour disappearing on dilution.

The ethyl acetate filtrate (*a*, above) was taken to dryness and the remaining solid extracted successively with cold alcohol and ethyl acetate. The pale orange-yellow residue was cyclotriselenium bisdibenzoylmethane,  $Se_3(C_{13}H_{10}O_2)_2$ , which reddened at 205° and melted at 220° with elimination of selenium; it was very sparingly soluble in benzene, separating therefrom in minute, bright yellow prisms containing no solvent of crystallisation. It was non-enolic towards ferric chloride and almost insoluble in chloroform, being thus distinguished from selenium dibenzoylmethane. With hydriodic acid in presence of ether, the triselenium compound yielded red selenium and orange diselenium bisdibenzoylmethane (XXVIII) identical with the product of the action of hydriodic acid on selenium dibenzoylmethane (p. 2442).

*Diselenium Bisdibenzoylmethane* (Formula XXVIII).

This substance was obtained by the action of aqueous hydriodic acid on selenium dibenzoylmethane in the presence of a mixture of ether and chloroform. In the absence of organic solvent, or in presence of chloroform alone, cold aqueous hydriodic acid had no

immediate action on powdered selenium dibenzoylmethane, but addition of ether caused instant liberation of iodine with production of *diselenium bisdibenzoylmethane*. The latter product, which remained partly in suspension and partly dissolved in the organic solvent, was rapidly separated, after removing free iodine by shaking with an excess of aqueous sodium thiosulphate. Prolonged contact with excess of hydriodic acid was found to cause complete reduction to red selenium and dibenzoylmethane. The crude orange product, which was very sensitive to boiling organic solvents, was purified by dissolving it in a little warm benzene and precipitating with light petroleum.

Diselenium bisdibenzoylmethane separated from a mixture of benzene and light petroleum in felted masses of slender, orange-yellow, prismatic needles, softening onwards from  $104^{\circ}$  and melting at  $116-118^{\circ}$ . It was readily soluble in chloroform or benzene and sparingly soluble in ether or petroleum. It possessed enolic properties, forming with cupric acetate an olive-green copper derivative soluble in chloroform, and giving a red coloration in a few seconds with ferric chloride (Found: C = 59.47; H = 4.06,  $C_{30}H_{22}O_4Se_2$  requires C = 59.56; H = 3.67 per cent.).

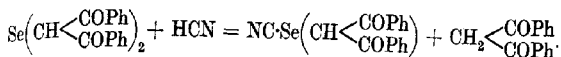
*Cyanoselenium Dibenzoylmethane* (Formula XXIV).

This substance was prepared either from selenium dibenzoylmethane or from selenium bisdibenzoylmethane:

(a) Powdered selenium dibenzoylmethane (0.8 gram), when left in contact with 10 c.c. of anhydrous hydrogen cyanide, dissolved in about three hours at laboratory temperature. After evaporation of the excess hydrogen cyanide, an oil was left, which soon became solid. The homogeneous product, cyanoselenium dibenzoylmethane, was obtained in colourless, prismatic needles by crystallisation from a mixture of benzene and light petroleum (b. p.  $40-60^{\circ}$ ). The addition to the hydrogen cyanide of one-fifth of its volume of pure ether entirely inhibits the above reaction, the selenium compound remaining undissolved.

(b) Selenium bisdibenzoylmethane was covered with anhydrous hydrogen cyanide and left for two days at the temperature of the laboratory. The solid dissolved and was replaced by a heavy oil. The excess of hydrogen cyanide was removed by evaporation in a desiccator, when a solid mixture of dibenzoylmethane and cyanoselenium dibenzoylmethane was left. These products were separated completely by dissolving the mixture in ether and shaking with aqueous cupric acetate. The dibenzoylmethane was precipitated as its copper derivative, the whole of the cyanoselenium dibenzoylmethane remaining in the ethereal layer. This product

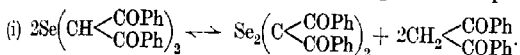
was identical with that obtained from selenium dibenzoylmethane. The following equation represents the change :



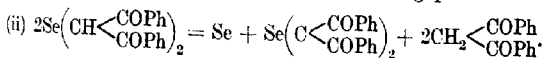
Cyanoselenium dibenzoylmethane closely resembled the corresponding derivatives from acetylacetone and benzoylacetone in appearance and odour, but differed from them in yielding no copper derivative with aqueous cupric acetate, although developing in a few minutes a blood-red coloration with ferric chloride. The compound softened slightly at 97° and melted at 100–101°; and was readily soluble in benzene or chloroform, moderately soluble in ether, and nearly insoluble in light petroleum. A cryoscopic determination of the molecular weight in benzene ( $c = 1.57$ ) gave  $M = 323$  (Found: Se = 23.60; N = 4.66.  $\text{C}_{16}\text{H}_{11}\text{O}_2\text{NSe}$  requires Se = 24.12; N = 4.27 per cent.;  $M = 328$ ).

*Transformations of Selenium Bisdibenzoylmethane under the Influence of Heat.*

When selenium bisdibenzoylmethane was caused to melt by heating in an oil-bath, and the molten substance maintained for half an hour at 140–145°, dibenzoylmethane was eliminated and an equilibrium represented by the following equation set up :



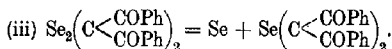
Cooling and examination of the mixture at this stage showed that about 50 per cent. of the original quantity of selenium bisdibenzoylmethane had undergone transformation, and that the dimeric selenium product represented on the right of the above equation consisted of *isoselenium dibenzoylmethane* together with a small proportion of *selenium dibenzoylmethane*. When, however, the temperature of the molten mass was allowed to rise above 150°, a further change set in, slowly at 155° and rapidly at 180°, whereby half the total amount of selenium present was set free with the formation of a new product, *selenium dehydrobisdibenzoylmethane*. The latter reaction being irreversible, the whole of the selenium bisdibenzoylmethane was ultimately transformed in the sense of the following equation, the yields of products being quantitative :



The intermediate compounds, *isoselenium dibenzoylmethane* and *selenium dibenzoylmethane*, when isolated and separately heated above their melting points, gave identical products, selenium and



selenium dehydrobisdibenzoylmethane, in the proportions demanded by the equation :



(a) In an experiment designed for the examination of the intermediate products, 3.99 grams of selenium bisdibenzoylmethane were heated for half an hour at 135–150° with stirring so that no selenium was set free. The yellow, viscous product was at once dissolved in chloroform and the liquid shaken with aqueous cupric acetate, 0.936 gram of copper dibenzoylmethane being obtained. The chloroform layer, on evaporation, left a yellow crystalline powder which contained *iso*selenium dibenzoylmethane and unchanged selenium bisdibenzoylmethane. Part of the former product was removed by fractional crystallisation from ethyl acetate; the mother-liquors were evaporated, the residues again heated, and treated as described above. In this manner, total amounts of 1.59 grams of copper dibenzoylmethane and 0.93 gram of pure *iso*-selenium dibenzoylmethane were accumulated. A proportion of unchanged selenium bisdibenzoylmethane was still present in the final fractions.

In a further experiment, selenium bisdibenzoylmethane was melted and heated at 146° for forty-five minutes. After separation of dibenzoylmethane and *iso*selenium dibenzoylmethane, the residual portion was examined by fractional crystallisation from ethyl acetate and benzene, when unchanged selenium bisdibenzoylmethane and a very small quantity of selenium dibenzoylmethane were isolated. These products were obtained in a state of purity and compared with analysed specimens.

*iso*Selenium dibenzoylmethane (formula XXVI) separated from ethyl acetate in rosettes of pale golden-yellow needles or flakes, which melted at 175–176° with elimination of red selenium. The mixed melting point with the isomeric selenium dibenzoylmethane showed marked depression.

An ebullioscopic determination of the molecular weight in benzene ( $c = 1.344$ ) gave  $M = 576$  (Found: C = 59.61; H = 3.32.  $\text{C}_{30}\text{H}_{20}\text{O}_4\text{Se}_2$  requires C = 59.75; H = 3.35 per cent.;  $M = 602$ ). The compound was rather sparingly soluble in ethyl acetate, less soluble in ether, but readily soluble in benzene or chloroform. It possessed no acid or enolic properties and did not give a coloration with ferric chloride. The behaviour of this compound when treated with hydrogen cyanide or with a mixture of aqueous hydriodic acid and ether was characteristic and quite different from that of its isomeride, selenium dibenzoylmethane (p. 2467); one

atom of selenium was set free and selenium dehydrobisdibenzoylmethane was produced. These reactions were catalytic, the hydrogen cyanide or hydriodic acid remaining unchanged.

*iso*Selenium dibenzoylmethane underwent the same transformation when heated to melting.

(b) In the following experiment the quantitative nature of the completed change (equation ii, p. 2469) was examined. Selenium bisdibenzoylmethane (3.00 grams) was heated from 160° to 185° during two and a half hours, no change of weight occurring; and the resulting orange glue, which solidified on cooling, was dissolved in chloroform and filtered from grey selenium. The chloroform filtrate was shaken with an excess of aqueous cupric acetate and the precipitated copper dibenzoylmethane collected. The chloroform layer, separated and allowed to evaporate, left an orange crystalline mass of selenium dehydrobisdibenzoylmethane, which was washed with a little cold ethyl acetate, dried, and weighed.

	Weight of free selenium.	Weight of copper dibenzoylmethane.	Weight of selenium dehydrobisdi- benzoylmethane.
Found .....	0.230 gram.	1.251 grams.	1.321 grams.
Calc. ....	0.226 "	1.458 "	1.494 "

*Selenium dehydrobisdibenzoylmethane* (formula XXVII) separated from ethyl acetate in small, refractive, bright orange crystals, melting without decomposition at 190–191°. Ebullioscopic determinations of the molecular weight in benzene gave  $M = 484$  ( $c = 0.941$ ), 449 ( $c = 1.536$ ) (Found: C = 68.77; H = 4.22; Se = 14.66.  $C_{30}H_{20}O_4Se$  requires C = 68.79; H = 3.85; Se = 15.13 per cent.;  $M = 523$ ).

The exceedingly small crystals of selenium dehydrobisdibenzoylmethane gave very poor reflections on the goniometer owing to face-curvature, and the elements were therefore evaluated graphically; although only approximate, they are sufficient to characterise the substance. The system is monoclinic with  $a:b:c = 2.10:1:1.40$ ,  $\beta = 99^\circ$ . The development is that indicated in plan by Fig. 8 and from a general point of view by Fig. 9, the forms being  $c(001)$ ,  $a(100)$ ,  $x(310)$ ,  $o(111)$ , and  $p(111)$ . Following are the mean results obtained from the largest crystal (0.3 mm. diameter):

	$x(310)$ .	$a(100)$ .	$c(001)$ .	$o(111)$ .	$p(\bar{1}11)$ .
$\phi$ .....	55.1°	90°	ca. 90°	31°	339°
$\rho$ .....	90	90	10°	60	50

The optic axial plane is  $b(010)$  and the negative acute bisectrix is inclined about 10° to the vertical in the acute angle  $\beta$ . An optic axis is visible through  $c(001)$ . Dispersion, abnormally strong,

$\rho > v$ . The compound was insoluble in water, moderately soluble in ethyl acetate, and readily soluble in ether, benzene, or chloroform. It formed intensely yellow solutions in organic media. The most noteworthy characteristic of this substance was its marked inertness to chemical reagents: it showed no acidic or enolic properties, being insoluble in cold 5*N*-sodium hydroxide and not reacting with ferric chloride or cupric acetate; it was unaffected by boiling concentrated hydrochloric acid, alkali bisulphites, ethereal aqueous hydriodic acid, or ethereal hydrocyanic acid; and was recovered unchanged after heating at 220° with calcium hydride. It was readily decomposed, however, by warm 50 per cent. potash with liberation of selenium and the production of acetophenone; it dissolved in cold concentrated sulphuric acid to a scarlet solution, being reprecipitated by the addition of water. The constitution

FIG. 8.

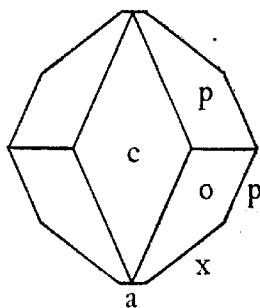
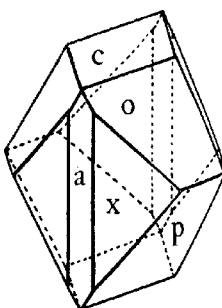


FIG. 9.



ascribed to selenium dehydrobisdibenzoylmethane was substantiated by reducing the compound with sodium amalgam in moist ethyl alcoholic suspension. Red selenium was set free, the odour of acetophenone was generated, and dibenzoylmethane (separated as its copper derivative) and benzoic acid were isolated from the solution in a pure condition. This result indicated initial reduction of the selenium compound to the expected products, dibenzoylmethane and selenium, followed by partial hydrolysis of the former in the presence of alkali.

Selenium dehydrobisdibenzoylmethane was also produced by heating selenium dibenzoylmethane or *isoselenium* dibenzoylmethane. Thus, 0.144 gram of selenium dibenzoylmethane, heated from 140° to 215° during ninety minutes, gave 0.019 gram of grey selenium and 0.124 gram of selenium dehydrobisdibenzoylmethane (calculated, 0.0189 gram and 0.125 gram, respectively); whilst 0.114 gram of *isoselenium* dibenzoylmethane, heated to 180° during

a similar period, gave 0.0156 gram of grey selenium and 0.0992 gram of selenium dehydrobisdibenzoylmethane (calculated, 0.0150 gram and 0.0990 gram, respectively).

Further methods of preparing selenium dehydrobisdibenzoylmethane consisted in shaking powdered isoselenium dibenzoylmethane with a mixture of ether and aqueous hydriodic acid, the transformation being unaccompanied by the liberation of iodine; and in leaving isoselenium dibenzoylmethane in contact with a large excess of anhydrous hydrogen cyanide for two days at the laboratory temperature. In these changes, an atom of selenium was liberated.

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#### CCXCIV.—*The Properties of Ammonium Nitrate. Part IV. The Reciprocal Salt-pair, Ammonium Nitrate and Sodium Chloride.*

By EDGAR PHILIP PERMAN.

THE system ammonium nitrate and sodium chloride is best considered as a special case of the reciprocal salt-pairs,  $\text{NH}_4\text{NO}_3 + \text{NaCl} \rightleftharpoons \text{NH}_4\text{Cl} + \text{NaNO}_3$ , with the assumption that the reacting salts need not be in molecular proportions.

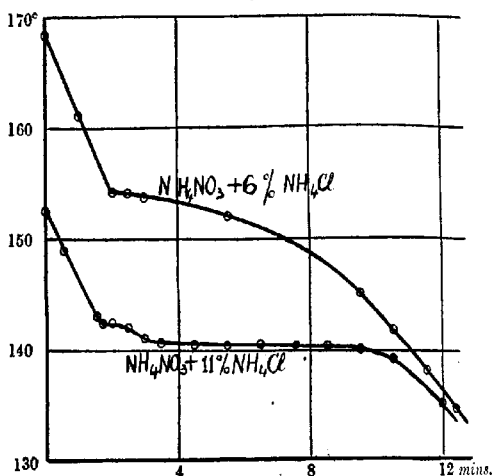
The ammonium nitrate is by far the most easily fusible of these salts, and readily acts as a solvent for the others, thus allowing, with very simple apparatus, the investigation of problems which would otherwise require metallic crucibles, furnaces, and pyrometers.

The problem of studying the chemical equilibrium in these salt-pairs may be divided into three parts: (1) Making the solutions of fused salts. (2) Cooling the mixture and observing the temperature when crystallisation begins. (3) Finding the nature of the crystals separating from the fused mass.

(1) The solutions were made as described in Part III (Early and Lowry, this vol., p. 963), except that for mixtures of high melting point an oil-bath was found necessary in order to avoid decomposition of the ammonium nitrate by local heating.

(2) The method of finding the crystallising point is described in Part III. An alternative method is worthy of mention, namely, that of cooling curves, of which examples are shown in Fig. 1. A slight arrest is shown at the crystallising point with ammonium nitrate and 6 per cent. of ammonium chloride, and a slight arrest, followed by a very marked one, with 11 per cent. of chloride, the latter being the freezing point of the eutectic mixture. The freezing points of such mixtures are always very well defined and can be more accurately determined in this way than by observing the formation of crystals.

FIG. 1.  
*Cooling curves.*

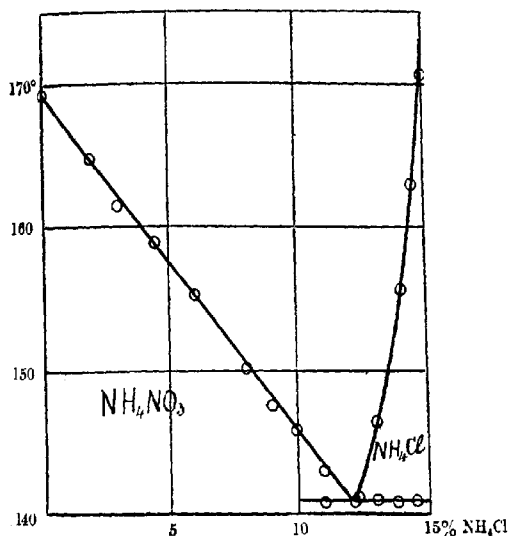


(3) The nature of the crystals separating was at first judged from what seemed most probable, a break in the melting-point curve indicating a change in the solid phase. The general diagram embodying the whole of the results was of great assistance in this matter. That these surmises were correct, has since been proved by an independent analytical method to be described in another paper. Analyses were made of the salts separating in each of the areas shown in the general diagram, and the results in every case corresponded with those given, with only a small experimental error. It should be noted that ternary mixtures may give curves not in accordance with the usual rules for two pure substances, and therefore great care must be taken in their interpretation.

*Binary Systems.*—These were investigated first; they are :  
 Ammonium nitrate and sodium nitrate, showing a eutectic at 20.1 per cent. of  $\text{NaNO}_3$ , freezing point  $121^\circ$ .  
 Ammonium nitrate and ammonium chloride, showing a eutectic at 12.1 per cent. of  $\text{NH}_4\text{Cl}$ , freezing point  $141^\circ$ .  
 Sodium nitrate and sodium chloride, showing a eutectic at 4.8 per cent. of  $\text{NaCl}$ , freezing point  $304^\circ$ .  
 Ammonium chloride and sodium chloride, unknown.  
 The first of these is described and illustrated in Part III.

FIG. 2.

*Ammonium nitrate + ammonium chloride.*



The second system is shown in Fig. 2. The most noteworthy point is the steepness of the right-hand branch. There are several secondary arrests at the eutectic temperature.

The third was determined somewhat roughly; it shows no special characteristics.

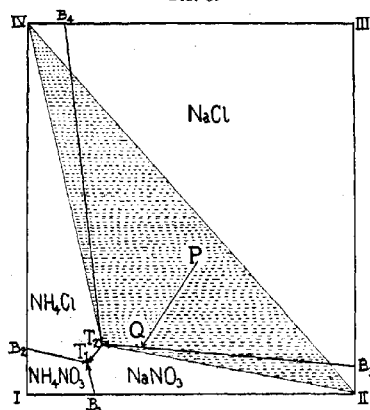
The fourth cannot be measured at the ordinary pressure owing to the volatilisation and dissociation of the ammonium chloride.

In addition to these, it will be shown later that ammonium chloride and sodium nitrate can exist in equilibrium together with liquid and vapour, thus forming a fifth binary system.

*Ternary Eutectics.*—There are two, a primary at  $112.4^{\circ}$ , the lowest freezing point observed in the whole of the experiments, and a secondary at  $133^{\circ}$ . The former was found by adding ammonium chloride to the ammonium nitrate-sodium nitrate eutectic, and was repeatedly observed as a secondary (or tertiary) arrest. The latter was near the second depression obtained on adding sodium nitrate to the ammonium nitrate-ammonium chloride eutectic and was definitely settled by the boundary lines of the sodium chloride, sodium nitrate, and ammonium chloride areas.

*General Diagram.*—It was necessary to put all results together on a general plan. A reciprocal salt-pair is really a ternary system,

FIG. 3.

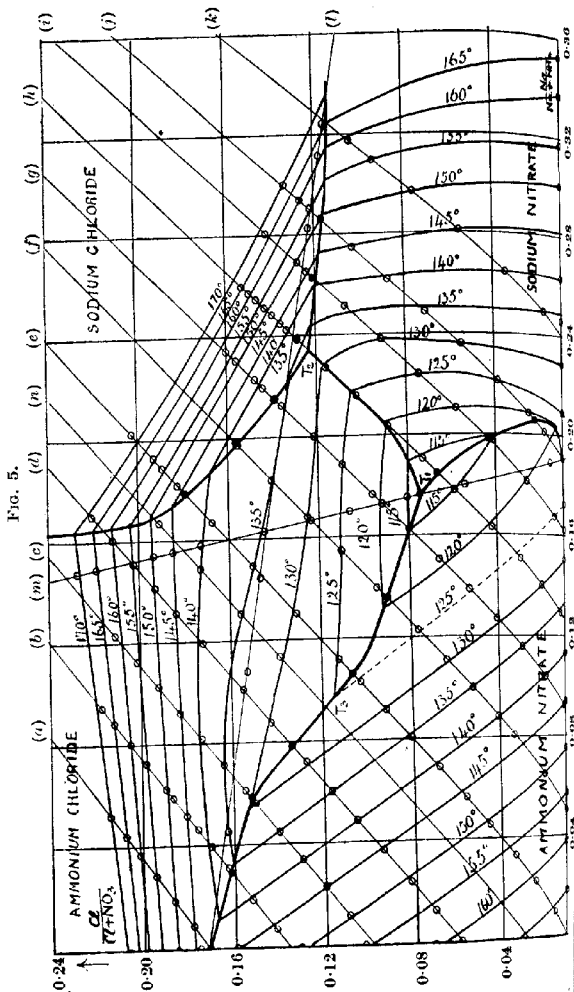


but since there are four radicals, the most convenient plan is a square, each corner of which represents one of the four salts in the system. This was devised independently, but was used by Jänecke in 1908 (*Z. physikal. Chem.*, **64**, 305). The ratios  $\text{Na}/\text{Na} + \text{NH}_4$  (sodium to total base) and  $\text{Cl}/\text{Cl} + \text{NO}_3$  (chlorine to total acid radical) are plotted as abscissae and ordinates respectively. The whole system in outline is shown in Fig. 3.  $B_1, B_2, B_3, B_4$  are the binary eutectic points in the order already given. The area actually investigated (in the left-hand bottom corner) forms a very small portion of the whole, the rest requiring unworkable temperatures. To fill in the details as far as possible a number of mixtures of ammonium nitrate with sodium nitrate or ammonium chloride were made, and sodium chloride was added in increasing proportions. The melting-point curves of most of these mixtures show





measured upwards from a horizontal base. The whole of the experimental results are given in an appendix.



*Discussion of Results.*—The diagram shows, at once, the equilibrium system. There are five binary systems in equilibrium (together with liquid and vapour): Ammonium nitrate and sodium

nitrate, ammonium nitrate and ammonium chloride, sodium nitrate and ammonium chloride, sodium nitrate and sodium chloride, ammonium chloride and sodium chloride.

There are two ternary systems in equilibrium (together with liquid and vapour): Ammonium nitrate, sodium nitrate, and ammonium chloride, and a subsidiary and less stable system, sodium nitrate, ammonium chloride, and sodium chloride.

On cooling a mixture corresponding with a point in any one of the areas, except the sodium chloride, the composition of the liquid will move towards one of the binary eutectics, then along that to the ternary point,  $112^{\circ}$ ; secondary and tertiary arrests of temperature illustrating this point were obtained repeatedly. If, however, the starting point is in the sodium chloride area, if in the shaded portions (Fig. 3), the composition will move first to one of the binaries enclosing that region, then to the ternary point,  $T_3$ ; it will not remain there, however, but travel towards  $T_1$ , where it will finally stop. On the other hand, if the starting point is outside the shaded area, it will stop at  $T_2$ , since there will not be enough ammonium nitrate to complete the double decomposition. Jänecke (*loc. cit.*) has classified the equilibrium systems, when no isomorphous mixtures or double compounds are formed, according to the position of the ternary points in the square. The case now described is evidently one of them, namely, 2, b. At  $125^{\circ}$ , ammonium nitrate undergoes a transformation from the  $\delta$  to the  $\epsilon$  form; this will therefore make a fifth area, and a subsidiary ternary point,  $T_3$ . The distinction is not well marked in these experiments, only one curve showing it; this is due probably to the lag in the transformation.

From the nature of the melting-point curves and from the general diagram, it may be concluded, therefore, that no isomorphous mixtures or double salts are formed.

The following systems of salt-pairs are also under investigation :

- (a)  $\text{NH}_4\text{NO}_3 + \text{KCl} \rightleftharpoons \text{NH}_4\text{Cl} + \text{KNO}_3$ .
- (b)  $2\text{NH}_4\text{NO}_3 + \text{Na}_2\text{SO}_4 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 + 2\text{NaNO}_3$ .
- (c)  $2\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 + 2\text{KNO}_3$ .

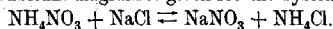
System (a) shows one ternary point at  $134.5^{\circ}$ , and mixed crystals ammonium nitrate and potassium nitrate; (b) shows a ternary point at  $121^{\circ}$ , and mixed crystals of ammonium nitrate and ammonium sulphate; (c) has at least one ternary point at  $137^{\circ}$ , and two more sets of isomorphous mixtures. Some systems of reciprocal salt-pairs forming isomorphous mixtures have been worked out by Jänecke, and it is proposed to deal with the whole question in a later paper.

*Summary.*

(1) The freezing point of ammonium nitrate is lowered from 169°:

- (a) to 141° by the addition of ammonium chloride;  
 (b) „ 121° by the addition of sodium nitrate;  
 (c) „ 112° by the addition of sodium nitrate and ammonium chloride.

(2) An equilibrium diagram is given for the system



This exhibits a ternary point at 133° for NaCl, NaNO<sub>3</sub>, and NH<sub>4</sub>Cl and a ternary eutectic at 112° for NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, and NH<sub>4</sub>Cl.

(3) No isomorphous mixtures or double salts are formed.

Most of this work was carried out at Guy's Hospital Medical School at the suggestion of Professor Lowry, to whom I am greatly indebted for kindly advice and criticism, and for facilitating the investigation in every way. I wish also to thank Mr. S. Philipson and Mr. J. W. Farmery for valuable assistance in the experimental work.

## APPENDIX.

*Freezing Points of Binary Mixtures.*

$\text{NH}_4\text{NO}_3 + \text{NaNO}_3$ . See Part III (*loc. cit.*).

Addition of NH<sub>4</sub>Cl to NH<sub>4</sub>NO<sub>3</sub> (Fig. 2).

NH <sub>4</sub> Cl .....	1.9	3.0	4.4	6.0	8.1	9.0	10.0%
F. pt. ....	164.9°	161.5°	158.8°	155.2°	150.2°	147.6°	146.0°
Arrest .....	—	—	—	—	—	—	—
NH <sub>4</sub> Cl .....	11.0	12.1	12.2	13.0	14.0	14.5	14.9%
F. pt. ....	143.2°	140.9°	141.2°	146.5°	155.6°	162.9°	170.6°
Arrest .....	140.7°	141.1°	141.3°	141.4°	141.0°	140.9°	—

Addition of NaCl to NaNO<sub>3</sub>.

NaCl .....	0.0	2.4	4.8	5.9	9.0%
F. pt. ....	312.0°	308.0°	304.0°	332.0°	380.5°

The freezing point falls to 304°, sodium nitrate separating, then rises rapidly, with separation of sodium chloride.

*Freezing Points of Ternary Mixtures.*

(a) Addition of NaCl to NaNO<sub>3</sub> + 12.1 per cent. NH<sub>4</sub>Cl.

NaCl .....	0.0	0.06	0.13	0.88	1.90	2.23	2.80	3.43%
F. pt. ....	141.0°	140.4°	141.0°	145.5°	152.5°	155.0°	159.5°	164.5°
Arrest .....	141.0°	—	140.5°	138.5°	135.5°	134.5°	132.5°	—

The freezing point (of ammonium chloride) rises continuously and the arrest (separation of ammonium nitrate and ammonium

chloride) falls continuously from the eutectic temperature at  $41^{\circ}$ .

(b) Addition of NaCl to  $\text{NaNO}_3 + 9.5$  per cent.  $\text{NH}_4\text{Cl}$ .

NaCl .....	0.0	0.84	1.43	3.09	3.58	4.54	5.31	7.05%
F. pt. ....	$148.0^{\circ}$	$143.6^{\circ}$	$140.5^{\circ}$	$140.0^{\circ}$	$142.5^{\circ}$	$148.0^{\circ}$	$153.0^{\circ}$	$166.5^{\circ}$
Arrest .....	—	—	—	$133.0^{\circ}$	$132.5^{\circ}$	$133.5^{\circ}$	—	—

The freezing point (of ammonium nitrate) falls from  $148^{\circ}$  to  $137^{\circ}$  and then rises when ammonium chloride separates instead; the horizontal arrest at  $133^{\circ}$  is an anomaly which has not been explained.

(c) Addition of NaCl to  $\text{NH}_4\text{NO}_3 + 6.92$  per cent.  $\text{NH}_4\text{Cl}$ .

NaCl .....	0.0	2.0	4.0	6.0	7.0	8.0	9.0	10.0%
F. pt. ....	$155.4^{\circ}$	$142.4^{\circ}$	$131.4^{\circ}$	$138.0^{\circ}$	$144.0^{\circ}$	$150.2^{\circ}$	$153.7^{\circ}$	$163.0^{\circ}$

The freezing point (of ammonium nitrate) falls to  $130^{\circ}$  and then rises (separation of ammonium chloride).

(d) Addition of NaCl to  $\text{NH}_4\text{NO}_3 + 4.09$  per cent.  $\text{NH}_4\text{Cl}$ .

NaCl .....	0.0	2.0	4.0	6.0	8.0	10.0	12.0%
F. pt. ....	$164.0^{\circ}$	$148.8^{\circ}$	$137.5^{\circ}$	$128.8^{\circ}$	$135.8^{\circ}$	$144.9^{\circ}$	$156.2^{\circ}$
				(min.)			

The freezing point falls to  $129^{\circ}$  and then rises as in (c).

(e) Addition of NaCl to  $\text{NH}_4\text{NO}_3$  (Fig. 4).

NaCl .....	2.0	4.0	6.0	7.0	8.0	10.0	12.0	14.0	14.5	15.0	16%
F. pt. ....	$157.9^{\circ}$	$146.4^{\circ}$	$135.1^{\circ}$	$129.7^{\circ}$	$123.6^{\circ}$	$129.9^{\circ}$	$137.1^{\circ}$	$143.8^{\circ}$	$153.6^{\circ}$	$161.7^{\circ}$	$172.2^{\circ}$
Arrest .....	—	—	—	—	—	$118.7^{\circ}$	$114.8^{\circ}$	$111.5^{\circ}$	—	—	$112.0^{\circ}$

(f) Addition of NaCl to  $\text{NH}_4\text{NO}_3 + 5.3$  per cent.  $\text{NaNO}_3$ .

NaCl ...	2.0	4.0	6.0	8.0	10.0	12.0	12.5	13.0	13.5	14.0%
F. pt. ....	$145.3^{\circ}$	$134.6^{\circ}$	$123.3^{\circ}$	$124.0^{\circ}$	$132.5^{\circ}$	$140.4^{\circ}$	$146.4^{\circ}$	$154.5^{\circ}$	$160.0^{\circ}$	$171.3^{\circ}$

The freezing point falls to  $120^{\circ}$ , then rises to  $141^{\circ}$ , after which sodium chloride separates as in (e).

(g) Addition of NaCl to  $\text{NH}_4\text{NO}_3 + 9.5$  per cent.  $\text{NaNO}_3$ .

NaCl .....	2.0	4.0	6.0	8.0	10.0	10.5	11.0	12.0%
F. pt. ....	$135.5^{\circ}$	$124.5^{\circ}$	$114.7^{\circ}$	$124.0^{\circ}$	$133.5^{\circ}$	$136.5^{\circ}$	$142.2^{\circ}$	$157.7^{\circ}$
				(min.)				

The freezing point falls to  $115^{\circ}$ , then rises to  $137^{\circ}$ , after which sodium chloride separates as in (e).

(h) Addition of NaCl to  $\text{NH}_4\text{NO}_3 + 13.3$  per cent.  $\text{NaNO}_3$ .

NaCl .....	0.00	1.13	2.47	4.69	5.00	5.42	6.84	8.22	9.74	10.20	10.45	11.25%
F. pt. ....	$136.5^{\circ}$	$130.0^{\circ}$	$123.0^{\circ}$	$113.5^{\circ}$	$112.5^{\circ}$	$115.0^{\circ}$	$121.5^{\circ}$	$128.0^{\circ}$	$134.5^{\circ}$	$144.0^{\circ}$	$147.0^{\circ}$	$164.5^{\circ}$
Arrest .....	—	—	—	—	$112.0^{\circ}$	$113.5^{\circ}$	$113.5^{\circ}$	$113.0^{\circ}$	—	$113.0^{\circ}$	$113.0^{\circ}$	—

The freezing point (of ammonium nitrate) falls to  $113^{\circ}$ , then rises (separation of sodium nitrate, not of ammonium chloride) to  $4^{\circ}$  P\*.

135°, after which sodium chloride separates. The arrest points are due to the crystallisation of the ternary eutectic.

(i) Addition of NaCl to  $\text{NH}_4\text{NO}_3$  + 17 per cent.  $\text{NaNO}_3$ .

NaCl .....	0.00	2.00	4.07	6.00	8.00	10.00	10.50%
F. pt. ....	127.0°	119.3°	118.2°	127.4°	133.3°	158.1°	167.3°

The freezing point (of ammonium nitrate) falls to 116°, then rises (separation of sodium nitrate) to 140°, after which sodium chloride separates.

(j) Addition of NaCl to  $\text{NH}_4\text{NO}_3$  + 20.1 per cent.  $\text{NaNO}_3$  (eutectic).

NaCl .....	0.50	0.99	1.42	1.96	2.91	3.85	4.76	6.54	8.26	9.00	9.50	10.40%
F. pt. ....	120.7°	119.7°	118.7°	121.5°	126.0°	129.2°	133.2°	140.4°	133.0°	164.4°	176.2°	
Arrest .....	—	—	118.3°	118.0°	115.5°	113.7°	112.2°	112.4°	111.6°	112.2°	—	112.2°

The freezing point (of ammonium nitrate) falls slightly to 119.7°, then rises (separation of sodium nitrate) to 149°, then sodium chloride separates. The arrest (separation of sodium nitrate with ammonium nitrate) falls progressively from 119° to the ternary eutectic at 112°.

(k) Addition of NaCl to  $\text{NH}_4\text{NO}_3$  + 25.1 per cent.  $\text{NaNO}_3$ .

NaCl .....	0.0	2.0	4.0	6.0	7.0	7.78%
F. pt. ....	132.0°	138.4°	144.9°	151.2°	155.4°	160.2°

The freezing point (of sodium nitrate) rises progressively.

(l) Addition of  $\text{NaNO}_3$  to  $\text{NH}_4\text{NO}_3$  + 12.1 per cent.  $\text{NH}_4\text{Cl}$  (eutectic).

$\text{NaNO}_3$ .....	2.0	3.0°	4.4	6.1	6.8	7.2	7.8	8.4	9.2	12.0	13.8%
F. pt. ....	138.1°	137.0°	135.7°	134.0°	133.0°	132.5°	132.7°	133.5°	133.9°	134.8°	134.8°
Arrest .....	—	135.3°	132.2°	—	129.4°	128.8°	—	127.6°	126.5°	—	—
$\text{NaNO}_3$ .....	16.0	16.9	20.0	21.0	23.6	24.3	27.0	29.9	35.1%		
F. pt. ....	134.4°	134.7°	—	134.0°	133.4°	133.5°	140.4°	147.8°	165.4°		
Arrest .....	115.2°	112.2°	—	—	112.1°	—	—	—	—		

The freezing point of the binary eutectic falls from 141° to 132°, rises to a shallow maximum at 135° and falls again to 133°; it then rises rapidly (separation of sodium chloride). The arrest falls progressively from 141° to the ternary eutectic at 112°.

(m) Addition of  $\text{NH}_4\text{Cl}$  to  $\text{NH}_4\text{NO}_3$  + 20.1 per cent.  $\text{NaNO}_3$  (eutectic).

$\text{NH}_4\text{Cl}$ .....	0.00	2.00	4.00	5.10	6.75	8.92	10.05	11.98	13.54	15.00%
F. pt. ....	121.5°	117.5°	114.2°	112.5°	122.5°	131.5°	134.5°	139.5°	148.5°	159.5°
Arrest .....	—	—	112.5°	113.0°	(min.)	112.5°	113.0°	—	—	—

The freezing point of the binary eutectic falls from 121° to the ternary eutectic at 112.5° (separation of ammonium nitrate), after which it rises (separation of ammonium chloride). As this section

of the diagram passes through the ternary eutectic, this gives very well marked arrests.

(n) Addition of NaCl to  $\text{NH}_4\text{NO}_3$  + 1.81 per cent.  $\text{NH}_4\text{Cl}$ .

	0.0	8.20	8.85	9.61	10.43	13.04%
NaCl .....	165.2°	128.3°	131.1°	133.1°	135.7°	145.1°
F. pt. ....						

*Ternary Points.*—The readings obtained for the ternary eutectics were as follow :

Curve (e) 111.5° 112.0°.

Curve (h) 112.0° 113.5° 113.5° 113.0° 113.0° 113.0°.

Curve (j) 112.2° 112.0° 111.6° 112.2° 112.0°.

Curve (l) 112.2° 112.1°.

Curve (m) 112.5° 113.0° 112.5° 113.0°.

The mean of these values is 112.4°.

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## CCXCV.—*The Propagation of Explosion Waves in Gases Contained in Tubes of Varying Cross-section.*

By COLIN CAMPBELL.

THE movements of the flames produced during the explosion of gaseous mixtures have been studied photographically by von Oettingen, Le Chatelier, Dixon, and others. Most of the experiments described by these investigators were conducted in tubes of uniform diameter; in other experiments, where the diameter altered, it did so gradually and only to a small extent.

The present investigation is an attempt to photograph explosion flames in different gaseous mixtures as these flames pass along tubes which are abruptly constricted or enlarged. Before describing the experiments, it is necessary, however, to refer briefly to some previously discovered characteristics of explosion waves in uniform tubes.

1. The velocity of the detonation wave in any given gaseous mixture is independent of the material composing the tube (Berthelot—see Dixon, *Phil. Trans.*, 1893, [A], 184, 99). Thus tubes of glass, metal, or rubber give approximately equal rates.

2. When a detonation wave meets the further, closed, end of the containing tube a wave of compression is sent back through the burning gases (Dixon, *ibid.*, 1903, [A], 200, 326). The velocity of this compression wave is approximately equal to that of a sound wave in the hot gases under the same conditions.

3. The velocity of the detonation wave is affected by the presence of a flexible junction (say of rubber) between two parts of the tube. At such a junction, the flame is damped down and takes some time to recover its original speed (Dixon, *ibid.*, p. 335).

4. It has also been found (author's unpublished results) that the diameter of the containing tube has some influence on the velocity of the detonation wave. With rapid mixtures, for example,  $C_2N_2 + O_2$ , the difference in the rates observed in tubes of 6 mm. and 19 mm., respectively, is small. If, however, a diluent gas is added and the rate consequently lowered, the difference in the rates observed in the two tubes becomes very considerable, for example, in the mixture  $C_2N_2 + O_2 + 2N_2$  the rates for the 6.5 mm. and 19 mm. tubes are, respectively, 2161 and 2238 metres per sec.

The present research may be conveniently divided into four sections, according as an explosion wave passes from one tube into (1) another tube of smaller diameter—"normal-narrow"; (2) a narrower tube and thence to a third of diameter equal to the first—"normal-narrow-normal"; (3) a wider tube—"normal-wide"; (4) a wider tube and then to one of original diameter—"normal-wide-normal."

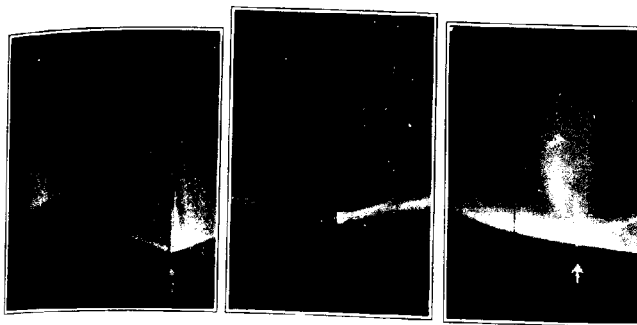
By a "normal" tube must be understood one in which the diameter is sufficient, but not greatly in excess of that required, to allow the detonation wave, travelling in any particular mixture, to assume its maximum velocity. On comparing the rates of several mixtures in tubes of different diameters, it was seen that a tube of about 10 mm. diameter would satisfy the conditions for a normal tube (Table I). Accordingly, tubes of diameter 10 mm. to 16 mm. were chosen as normal tubes.

TABLE I.

Velocities of explosion waves in tubes of different diameters.

Mixture.	6 mm.	9 mm.	12.7 mm.	15 mm.
$2H_2 + O_2$ .....	—	2321	—	2328
$2H_2 + 4O_2$ .....	—	1927	1921	—
$2H_2 + O_2 + 3N_2$ .....	—	2055	—	2089
$C_2N_2 + O_2 + 2N_2$ .....	2161	2230	2230	—

As far as possible the tubes were constructed entirely of glass and the different portions of the tube were fused together at the common junction. In all cases this junction was so constructed that the change in diameter was very abrupt and not a gradual widening or narrowing. In the case of very wide tubes, it was not possible to construct them all in one piece and a special device (described later) had to be adopted in order to overcome this difficulty without introducing any flexible joint. In some experiments



A 3.--Detonation wave passing into a narrower tube. B 1. Flame velocity increased at junction with narrower tube. D 3. Tube shattered. Apparent decrease in flame velocity.



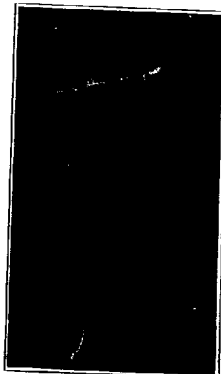
E 1. Flames in normal narrow normal tube.



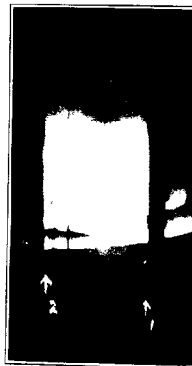
E 2. Same tube as E 1. Stopper set in position.



L 1. Detonation wave retarded at junction with stopper.



L 6. Retarded flame checked by stopper.



L 7. Retarded flame checked by stopper.





the very wide tube was made of stout glass tubing, whilst in others metal tubes were used; the results did not indicate any difference in the behaviour of the flames due to these differences in material. In each series of experiments the normal tube was joined to a length (several metres) of lead pipe of the same diameter; this lead pipe carried a sparking-piece and brass tap at its further end. The initial movements of the flame preceding the formation of the detonation wave took place in the lead pipe, and the flame which entered the glass tube was quite steady—in fact the detonation wave itself.

The movements of the flames were analysed on a rapidly moving wheel carrying a photographic film—like the apparatus described in a previous research (*Proc. Roy. Soc.*, 1914, [A], 90, 506). Slight variations were made in the method of driving the wheel and in the addition of a device for timing its speed. The explosion tubes were placed horizontally and the flames traversed them from left to right. The film was moving vertically downwards at the point where it received the image of the flame; the photographs, therefore, show lines which are compounded of two velocities at right angles and in every case the print of the film indicates a line starting from the right-hand bottom corner and inclined at an angle to the horizontal. In most of the experiments the flame in the normal tube was visible and its velocity known; the speed of the wheel can therefore be calculated. In all the photographs thin, dark, vertical lines appear; these are caused by strips of black paper fastened across the front of the tubes at distances of 10 cm., measured from the junction of the two tubes. These lines serve as reference marks and are useful in measuring the photographs. In order to obtain the same width of flame in two tubes of different diameters, black paper was fastened round both tubes, leaving at the front only a horizontal opening of equal width along the whole length of tube photographed.

#### I. "Normal-narrow."

Since the detonation wave is the wave of maximum velocity which can traverse a particular gaseous mixture at a definite temperature and pressure, a sudden diminution in the diameter of the containing tube cannot cause any increase in velocity unless one or both of these factors are altered. It is possible that the increased lateral pressure exerted by the walls of the tube might cause an increase in rate. This effect is likely to be very small, however, for Dixon (*Phil. Trans.*, 1893, [A], 184, 179) has shown that the rate of the detonation wave in one particular gaseous mixture was only increased from 2775 metres per sec. to 2872 metres per sec. when the initial pressure was raised from 500 mm. to 1500 mm.

It is more probable that a *decrease* in velocity should occur owing to the great cooling effect of the walls of the tube—especially in those cases where the diameter is very small. It is conceivable that the two effects—one of increase of velocity and one of decrease—might compensate one another in the case of one particular mixture, but it is unlikely that it would happen in a number of different mixtures.

Accordingly, five different gaseous mixtures were used in four different tubes (named series A, B, C, D respectively). In Table II the dimensions of the tubes used in these experiments are given and in Table III the results of the various experiments.

TABLE II.

Series.	Dimensions of tubes.		
	Normal tube.	Narrow tube.	Length in cm.
	Diam. in mm.	Diam. in mm.	
A	16	9	33
B	15	7	33
C	16	5	33
D	9.5	6	33

TABLE III.

Series.	No.	Mixture.	Change in rate at junction.	Remarks.
A	1	$2\text{H}_2 + 3\text{O}_2$	None	
	2	$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$	"	Tube shattered.
	3	$2\text{H}_2 + 3\text{O}_2$	"	
	4	$2\text{H}_2 + 3\text{O}_2$	"	Cork maintained in position.
B	1	$\text{H}_2 + \text{O}_2$	None	
	2	$\text{H}_2 + \text{O}_2$	"	
	3	$2\text{H}_2 + 3\text{O}_2$	Slight increase	} Probable obstruction in the lead pipe.
	4	$2\text{H}_2 + 3\text{O}_2$	" "	
	5	$2\text{H}_2 + 3\text{O}_2$	" "	
	6	$3\text{CS}_2 + 5\text{O}_2$	None	
	7	$3\text{CS}_2 + 5\text{O}_2$	"	
C	1	$2\text{H}_2 + 3\text{O}_2$	None	
	2	$3\text{CS}_2 + 5\text{O}_2$	"	
	3	$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$	"	
	4	$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$	"	
	5	$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$	Slight increase	Tube shattered.
	6	$2\text{H}_2 + 3\text{O}_2$	None	
	7	$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$	Slight increase	Tube shattered.
	8	$2\text{H}_2 + 3\text{O}_2$	None	
D	1	$2\text{H}_2 + 3\text{O}_2$	None	
	2	$2\text{H}_2 + 3\text{O}_2$	"	
	3	$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$	Slight decrease	Tube shattered.

In most of the experiments, the explosion wave had the same velocity in the normal and the narrow tubes. In experiment D 3 the tube was shattered; this may account for the apparent decrease in velocity of the flame when it had traversed about 10 cm. of the

narrow tube. In those few experiments where there was an increase in velocity at the junction (see Table III), the *initial* flame was not constant, but was increasing in speed as it approached the junction. It is probable that the detonation wave had been damped down by some slight obstruction in the lead tube and had not again reached its maximum velocity when it was photographed. At the junction the high pressure produced initiated a wave—probably the detonation wave—in the narrow tube, and also gave an intense return wave in the partly burnt and still burning gases in the normal tube (B 4).

It is established, therefore, that when a detonation wave, travelling in a tube of uniform diameter, suddenly enters a much narrower tube, there is no appreciable change in velocity at the junction. In the mixtures used, the detonation wave can traverse at least 30 cm. of glass tubing 5 mm. or more in diameter.

Attention must also be directed to a slower secondary wave which follows the detonation wave starting from the junction and moving towards the end of the narrow tube (see photograph A 3). It is probably a wave of compression and is caused by forward moving gas in the wake of the detonation wave increasing the pressure at the junction. This pressure tends to release itself—forward in the narrow tube and backwards in the wider tube. Since the gas is already moving forward in the narrow tube, but is almost stationary in the wide tube, the forward wave moves faster than the backward wave.

The return wave of compression produced when the initial detonation wave collides with the cork, is clearly seen in all the photographs. In some cases, it is slightly curved, owing to the movements of the gas *en masse*, but in most cases is quite straight—indicating a constant velocity. In Table IV, the measurements of the tangents of the angles which the reflected waves in the normal and narrow tubes make with the horizontal are compared.

TABLE IV.

Mixture.	Photo.	Tangents of angles of return wave in	
		Normal tube.	Narrow tube.
$2\text{H}_2 + 3\text{O}_2$	A 1	0.33	0.36
"	A 3	0.33	0.34
"	A 4	—	0.34
"	C 6	0.32	0.36
"	C 8	0.35	0.37
$3\text{CS}_2 + 5\text{O}_2$	B 6	0.44	0.45
"	B 7	0.41	0.46
"	C 2	0.37	0.40
$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$	C 3	0.26	0.27
"	C 4	0.28	0.30

The individual values depend on the velocity of the photographic wheel as well as on the velocities of the flames, but the table brings out the fact that the return wave in the normal tube is more rapid than that in the narrow tube—the velocities of these waves being inversely proportional to the tangents of the angles. This difference in velocity may be due to the fact that in the normal tube the gas is almost stationary, whereas in the narrow tube it is still moving forward towards the closed end. Also, the narrow tube may cool the gas more rapidly than the normal tube.

## II. "Normal-narrow-normal."

It has been shown by Le Chatelier (*Ann. Mines*, 1883, 4, 319) that a mixture of methane and air (containing 10·4 per cent. of the former) will not propagate a flame in glass tubes of 3·2 mm. diameter, and that metal tubes prevent the propagation more effectively than glass tubes of the same diameter. Payman and Wheeler (T., 1918, 113, 656) have shown that 2 cm. of brass tubing (of diameter up to 8 mm.) will prevent a slow flame in a mixture of methane and air from spreading into a second wide vessel. If the flame was allowed to attain a somewhat higher velocity (that is, by permitting it to travel a greater length in the wider vessel before it met the narrow tube), a greater length of brass tubing was required to prevent it spreading into the second vessel. The flames used in these experiments were moving with a velocity less than 100 cm. per second and therefore the cooling effect of the walls of the vessel was considerable.

In the experiments described in this paper, the flames were travelling with a velocity of more than 2000 metres per second; the temperature of the gases was raised more suddenly than in Payman and Wheeler's experiments, and the time of passage of the flame much shorter. It is not surprising, therefore, to find that the detonation waves in various mixtures of gases can traverse quite considerable distances along a very narrow tube and spread into a second wide vessel. The tubes used were constructed entirely of glass, the two end ("normal") tubes being fused to the central ("narrow") tube. The normal tubes were of equal diameter, approximately 16 mm., in all the experiments. One of them was joined to a lead coil (of equal bore), at the far end of which the gases were fired; the other normal tube was varied in length between 19 cm. and 31 cm. The central (narrow) tube was varied in both length and diameter, as the following table shows.

In all these experiments the mixture  $2\text{H}_2 + 3\text{O}_2$  was employed. This particular one was chosen because, whilst it gave a fairly good light, the pressures produced did not shatter the apparatus

TABLE V.

Dimensions of tubes used in "normal-narrow-normal."

Series.	Narrow tube.		2nd normal tube. Length (cm.).
	Diam. (mm.).	Length (cm.).	
E	5.5	4.5	24
F	5.5	9.0	27.5-31
G	5.5	19.0	31
H	2.0	21.0	19
J	2.0	32.5	23.5
K	1.5	40.5	23.7

as often as the less diluted but more actinic mixtures would have done. The end of the tubes was closed by a tightly fitting cork, which was usually allowed to blow out; a few experiments were performed with the cork held firmly in position; this made little difference, if any, to the general phenomena observed.

In experiment E 1 (photograph reproduced), the detonation wave, travelling at uniform speed, collided with the junction wall (at  $\uparrow_1$ ) through which the narrow tube continued. Here an intense wave of reflection was sent back, but the original wave passed through the narrow tube with unchanged velocity. At the second junction, the wave became much less luminous and travelled forward at a velocity which appeared almost constant, but was much less than the velocity of the original wave. At a point about 21.5 cm. from  $\uparrow_2$ , the flame was checked and an intense wave—possibly of reflexion—passed back through the burning gases. This return wave appears to have been caused by a wave of compression which had *preceded* the flame and had suffered reflexion from the cork—situated 24 cm. from  $\uparrow_2$ . At the point of collision between the pressure-wave and flame, the latter continued to advance towards the cork, which was finally forced out.

The return wave in the burning gases was nearly constant in velocity and where it collided with the junction wall at  $\uparrow_2$  the luminosity was very great—suggestive of a very high pressure. At  $\uparrow_2$ , part of the wave continued its journey into and through the narrow tube and part was again reflected.

This photograph (E 1) is similar to many others taken in tubes of similar shape but of different dimensions. Photograph E 2 shows the effect of keeping the cork firmly fixed in position. The confined gas continued to burn for some time and was crossed and recrossed by waves of pressure—reflected in turn from the cork and from the junction-wall  $\uparrow_2$ . An increase in length of the middle narrow tube to 9 cm. and then to 19 cm. did not appreciably affect the velocity of the flame in this narrow tube (F and G experiments).

When the diameter of the narrow tube was reduced to 2 mm.,

the amount of light given out was very small and few good photographs were obtained. The wave in this narrow tube still appeared constant in velocity even when it traversed a length of 32 cm. With further increase in length (to 40.5 cm.) and further diminution in diameter (to 1.5 mm.), no good photograph was obtained, but the flame passed through the narrow portion and ignited the gas in the further tube.

The velocities of the retarded flames in the end tube can be calculated from the velocity in the centre tube and from the measurements of the angles formed by these flames in the photograph. The velocity of the flame in the centre tube is assumed to be that of the detonation wave in the mixture used ( $2\text{H}_2 + 3\text{O}_2$ ) and is probably about 2120 m. per sec.

The values of  $\tan \alpha$  and  $\tan \beta$  (in Table VI) are calculated from the measurements of the angles (in the photographs) formed by the flame in the narrow and normal (end) tubes respectively.

TABLE VI.  
Measurement of angles made by flame edges.

Experiment.	$\tan \alpha$ .	$\tan \beta$ .	$\frac{\tan \alpha}{\tan \beta}$ .	Velocity of retarded flame in m. per sec.
E 1	0.13	0.53	0.25	530
E 2	"	0.52	0.25	530
F 1	"	0.44	0.29	610
F 3	"	0.54	0.24	510
F 6	"	0.51	0.25	530
F 7	"	0.50	0.26	560
F 8	"	0.49	0.27	580
F 9	"	0.50	0.26	560
G 1	"	0.44	0.29	610
G 2	0.14	0.48	0.29	610
			Mean	560
H 1	0.13	0.50	0.19	410
J 2	0.15	0.74	0.20	430
J 3	0.14	0.72	0.20	430
			Mean	420

These results appear to indicate that where the expansion at  $\uparrow_2$  is from a 5 mm. tube to a 10 mm. tube the velocity of the retarded flame is about 560 m. per second, but where the expansion is greater (that is, from 2 mm. to 10 mm.) the retarded flame is slower, namely, 420 m. per second.

We may summarise the results of experiments in normal-narrow-normal tubes as follows:

1. An explosion wave in the mixture  $2\text{H}_2 + 3\text{O}_2$  can pass from a normal through a narrow and into a second normal tube. In glass tubes, the middle section may be as narrow as 1.5 mm. and flames will pass through a length of at least 40 cm. of this narrow

TABLE VII.  
Measurements of flame angles.  
Mixture  $2\text{H}_2 + 3\text{O}_2$ .

Expt.	Diam. of wide tube in mm.	Initial wave. Tan $\alpha$ .	Retarded flame in		
			1st 10 cm. Tan $\beta_1$ .	2nd 10 cm. Tan $\beta_2$ .	3rd 10 cm. Tan $\beta_3$ .
L 1	22	0.15	0.37	0.37	
L 2	22	"	0.36	"	
L' 3*	22	0.16	0.37	"	0.37
M 1	35	0.16	0.56	0.57	0.57
M 2	35	0.17	0.52	0.52	0.52
O 1	62	0.15	0.68	0.85	
O 2	62	0.13	0.66	0.67	0.67
O 3	62	"	0.68	0.69	
Q 1	85	0.13	0.55		
Q 2	85	0.12	0.60		
Q 3	85	0.14	—		
Q 4	85	0.15	—		
Q 5	85	0.12	0.61		
R 3	91	0.16	0.78 †	0.78 †	
R 5	91	"	0.75 †	0.75 †	

\* L' 3. Length of wide tube = 70 cm.

† Mean values of 20 cm.

Mixture  $\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$ .

Expt.	Diam. of wide tube in mm.	Initial wave. Tan $\alpha$ .	Retarded flame in		
			1st 10 cm. Tan $\beta_1$ .	2nd 10 cm. Tan $\beta_2$ .	3rd 10 cm. Tan $\beta_3$ .
L 3	22	0.15	0.45	0.60	—
L 4	22	0.16	0.47	0.59	0.61
L 5	22	0.15	0.43	"	0.67
L 6	22	0.16	0.45	0.64	0.70
L' 1*	22	"	0.46	0.58	0.69
M 3	35	0.16	0.55	0.78	0.85
N 1	45	0.16	0.65	0.79	0.81
N 2	45	—	0.62	1.1	
P 2	65	0.12	0.65	0.94	
R 1	91	0.16	0.86	0.97	
R 2	91	0.14	0.84	1.14	
R' 1*	91	—	0.89	0.91	1.10

\* Length of wide tube in L' 1 and R' 1 = 70 cm.

tube. The luminosity of the flames is small in these very narrow tubes.

2. The explosion wave in a tube of diameter not less than 2.0 mm. suffers no appreciable change in velocity over a length of at least 30 cm.

3. The explosion wave suffers a diminution in velocity when it enters the end tube, and this retarded flame is preceded by a wave of compression.



## III. "Normal-wide."

The experiments in II have shown that a considerable retardation of the flame occurs at the point where the flame, having travelled through a very narrow tube, suddenly debouches into a wider tube. The experiments to be described here, show that the detonation wave itself, travelling in a tube 10 mm. in diameter, is similarly retarded at the junction ( $\dagger$ ) with a much wider tube (photograph L 1). Photographs have been obtained of this retarded flame in tubes, the narrow part of which was always 10 mm. wide, whereas the wide part differed in diameter. Since some of the flames after retardation were not constant in velocity, the angles made by these flames in each 10 cm. section of the wide tube (counting from the junction) have been measured separately and are called  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , respectively (Table VII). Except where indicated, the wide tube was approximately 30 cm. long.

From the mean values of  $\tan \alpha$  and  $\tan \beta$ , and from the known values of the initial explosion waves in the two mixtures, the velocities of the retarded flames have been calculated (Table VIII).

TABLE VIII.  
Velocity of Retarded Flame.

Mixture.	Diam. of wide tube in mm.	Mean $\tan \alpha$ .	Mean $\tan \beta_1$ .	Velocity of flame in m. per sec.
$2H_2 + 3O_2$	22	0.15	0.37	890
"	35	0.165	0.54	640
"	62	0.135	0.67	430
"	85	0.125	0.60	450
"	91	0.16	0.78	440
			Mean $\tan \beta_2$ .	
$C_2N_2 + O_2 + 2N_2$	22	0.16	0.60	590
"	35	0.16	0.78	455
"	65	0.12	0.80 *	340
"	91	0.15	1.06	310

\* This figure is mean  $(\tan \beta_1 + \tan \beta_2)/2$  because the flame edge is curved.

The results show the very great retardation produced at the junction. The velocity of the retarded wave is apparently dependent on the particular explosive mixture used and on the relative diameters of the wide and the narrow tube. Under the conditions of these experiments, the 91 mm. tube appears to cause very little more retardation than a 65 mm. tube, and a limit has probably been reached.

It may be assumed that the gases in the wave-front (continuously fired by adiabatic compression) are at a very high temperature and pressure. At the junction, the great lateral pressure exerted by the sides of the tube is suddenly removed, the hot gases are

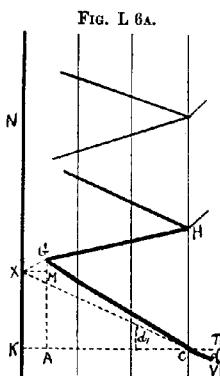
free to expand in every direction and are consequently cooled. The phenomenon may be compared with the expansion through a nozzle of a gas under pressure. The greater the difference in the diameters of the normal and narrow tubes, the greater will be the expansion and consequent retardation of the flame. Experiments performed in wide tubes of greater length than 30 cm. show that the retardation of the flame at the junction is the same as for a shorter tube of the same diameter; a few photographs, taken further along a tube 70 cm. in length, show that the flame is again gathering speed and is probably on the way to set up the explosion wave once more.

The means adopted to close the end of the tube did not affect the amount of retardation of the flame. This was shown by experiments where the end was closed by a cork or rubber stopper loosely inserted or firmly inserted, by a metal disk lightly cemented over the end, or even by a piece of paper gummed over the end. In those experiments where a rubber stopper was tightly inserted and consequently less air was drawn into the tube, the mixture remained luminous for a longer time.

A few experiments were performed at pressures less than atmospheric. In two experiments at 370 mm. pressure, the flame in the mixture  $2\text{H}_2 + 3\text{O}_2$  did not travel very far in the 10 mm. tube, whereas at 500 mm. the flame was visible and the stopper violently ejected, but no photograph was obtained. With the mixture  $2\text{H}_2 + \text{O}_2$ , the flame died out in the 10 mm. tube when the pressure was 270 mm., but at 400 mm. pressure the explosion wave—probable velocity 2800 metres per second—was retarded at the junction as in the experiments at atmospheric pressure. The retarded flame had a velocity in the 91 mm. tube of about 560 metres per second.

In photograph L 6, the retarded flame is seen to have been checked at a point 26 cm. from the junction (†), the stopper of the tube being 3.5 cm. further on. In another experiment where the advancing flame was still slower, it was stopped at a point 23 cm. from the junction, the stopper being 9 cm. further on. It is believed that this checking of the flame is caused by a wave of pressure which has preceded the retarded flame, has been reflected from the closed end of the tube, and on its return journey has checked the flame and become visible in the hot gases behind the wave-front. An attempt has been made to calculate the velocity of this pressure-wave in different experiments, assuming (1) that the pressure-wave starts its independent existence at the junction, and (2) that it is reflected from the stopper without loss of velocity—a condition which may only obtain with waves of small amplitude.

In Fig. L 6A (taken from L 6), the line  $CX$  represents the probable course traced by the pressure-wave as it advances from the junction  $C$ , meets the end of the tube at  $X$ , and is reflected along  $XG$ , col-



liding with the retarded flame at  $G$ . The angles  $CXM$  and  $MXG$  are made equal, and therefore the position of  $M$ , and consequently of  $X$ , can be determined from measurements of the photograph. It can be shown that  $MG/XM = \tan \alpha$ , and also that  $V_F = (\tan \alpha / \tan \alpha_1) V_F$ , where  $V_F$  = velocity of the pressure-wave,  $V_F$  = velocity of the initial flame, and  $\alpha$  the angle between the initial flame and the horizontal.

In Table IX, values of  $V_F$  in different experiments have been calculated from measurements of the corresponding photographs by means of the above formula.

TABLE IX.  
Velocities of pressure-waves.  
Mixture  $2H_2 + 3O_2$ .

Expt.	Diam. of wide tube in mm.	$\tan \alpha$ .	$\tan \alpha_1$ .	$V_F$ in m. per sec.
L 1	22	0.15	0.35	910
L 3	"	"	0.32	980
M 1	35	0.16	0.40	840
M 2	"	0.165	"	870
O 1	62	0.15	0.48	670
O 2	"	0.14	0.46	640
O 3	"	"	0.47	630

Mixture  $C_2N_2 + O_2 + 2N_2$ .

L 3	22	0.15	0.43	780
L 4	"	0.16	0.44	800
L 5	"	0.15	0.42	790
L 6	"	0.16	0.43	820
M 3	35	"	0.51	690
N 1	45	"	0.58	610
N 2	"	"	"	610
P 2	65	0.15	0.65	510
R 1	91	"	0.70	480
R 2	"	"	0.71	460

The velocity of sound in the mixture  $2H_2 + 3O_2$  at  $16^\circ$  is about 410 m. per second calculated by the Laplace formula, the value of  $\gamma$  being assumed to be 1.40. The value of  $\gamma$  for cyanogen probably lies between the limits 1.25 and 1.30, giving values of  $\gamma$  for the

mixture  $C_2N_2 + O_2 + 2N_2$  of 1.36 or 1.37. Calculated on the latter value, the velocity of sound in this mixture is about 306 m. per second. The velocities of the pressure-waves in the preceding tables are seen to be much faster than the velocity of sound in the same mixture. Where the diameters of the wide and the narrow tubes are very different, the pressure-wave appears to move about 50 per cent. faster than the sound wave; where the diameters are more nearly alike, the pressure-wave is a concussion wave of which the velocity is more than double that of sound. If these pressure-waves lose velocity on reflexion, as stated by Crussard (*L'Onde de Choc*, p. 34), their velocities will be higher than the values given in Table IX.

When a quite narrow tube—5 mm. in diameter—debouches into a wider tube of 16 mm. diameter, the pressure-wave produced in the latter travels at about 640 m. per second (mixture  $2H_2 + 3O_2$ )—a value which is near the rate found in experiments O 1, O 2, O 3 (Table IX).

The course followed by the wave of pressure after its collision with the flame is seen to advantage in photograph L 6 (Fig. L 6A). The wave proceeded from left to right through the burning gases at nearly constant velocity until it reached the junction, where it was almost completely reflected; in its return journey towards the end of the tube, it overtook the flame front, helped it along, and was again reflected from the stopper. Similar phenomena were observed in experiments with different mixtures and under different conditions. Measurements of the velocities of these waves of pressure were made in nineteen different experiments, and a number of deductions of a general character are possible. It was found, of course, that the velocity of the wave moving in the burning gases (for example, *GH* in Fig. L 6A) was very much greater than the calculated velocity of the pressure-wave (in the cold gases) which produced it (*CX* or *XG*). Higher values of *CX* gave higher values for *GH*, but this relationship only held for each single mixture. At *H*, part of the pressure-wave was reflected, but in almost every case there was a considerable loss of velocity at this point. This loss was most noticeable where the difference in the diameters of the wide and the normal tube was small; where the junction approximated to an unpierced disk, the reflexion of the pressure-wave was almost complete. The gas itself was, almost certainly, in violent motion and the velocity of the pressure-wave moving in this gas would be increased or diminished by the direction and amount of the movement of the medium. The velocity of the pressure-wave would also be dependent on the temperature of the flame through which it was passing and this temperature would

vary, not only with the mixture, but also with the cooling (by expansion) at the junction.

#### IV. "Normal-wide-normal."

A number of experiments were performed in tubes containing a central ("wide") portion between two narrower ("normal") portions. The central portion was about 12 cm. long and 47 mm. in internal diameter. The end portions were 10 mm. in diameter, one end being fitted to the lead tube and firing-piece and the other being closed in the usual way. Three different mixtures were used, namely,  $3\text{CS}_2 + 5\text{O}_2$ ,  $2\text{H}_2 + 3\text{O}_2$ , and  $2\text{H}_2 + \text{O}_2$ . In each case, the initial explosion wave was retarded at the first junction ( $\uparrow_1$ ) (see photograph S 4—mixture  $2\text{H}_2 + \text{O}_2$ ) and moved with almost constant velocity through the central wide tube. In the  $3\text{CS}_2 + 5\text{O}_2$  mixture, the retarded flame soon gathered speed again. At the second junction ( $\uparrow_2$ ) there was a great increase in the intensity of the light. The wide portion of the tube was so short that the retarded flame and the pressure-wave which preceded it were reflected from ( $\uparrow_2$ ) at almost the same instant, and it was impossible to distinguish their separate effects. A very rapid flame goes forward from ( $\uparrow_2$ ) in the end tube. This appears to be the detonation wave, which has been re-started at the junction ( $\uparrow_2$ ).

#### Summary.

The following general conclusions can be drawn from all the experiments with the different tubes:

- (a) An explosion wave does not change its velocity appreciably when it passes into a narrow tube, whether this narrow tube is closed at the further end or whether it opens again into a wider tube. The distance over which this flame can travel will probably depend on the material of the tube, but very narrow glass tubes (about 2 mm. in diameter) will allow the flame in the mixture  $2\text{H}_2 + 3\text{O}_2$  to travel at least 40 cm. without appreciable retardation.
- (b) An explosion flame is suddenly retarded at any point where a sudden expansion of hot gases may occur. In some gaseous mixtures, this flame then moves at a fairly constant velocity for some distance; in others, it continues to be retarded. Probably it finally gains speed and reproduces the detonation wave. The retardation of a detonation wave as it passes through a flexible joint between two rigid tubes (as recorded by Dixon, *Phil. Trans.*, 1903, [A], 200, 334) is probably due to a sudden expansion at the junction. Where the joint is smooth and rigid and the tubes of equal diameter, no expansion occurs, and therefore no retardation takes place.

(c) The retarded flame is preceded by a compression wave, more or less rapid according as the expansion has been small or great, and this, after collision with the closed end of the tube, is reflected and checks the advancing flame.

(d) The rates of the retarded flame and of the preceding pressure-wave are dependent on the gaseous mixture, the relative sizes of the different portions of the tube, and possibly the initial pressure. The greater the difference between the diameters of the two portions of the containing tube, the less the velocities of the retarded flame and of the preceding pressure-wave in any one mixture. These velocities reach a lower limit in a very wide tube.

#### EXPERIMENTAL.

*The Tubes.*—In experiments with tubes of diameter less than 65 mm., these tubes were made entirely of glass, the different sections being fused together. When the diameter exceeded 65 mm., several kinds of tubes were employed. In the earlier experiments, a tube of mild steel was used; it was open at one end and closed at the other except for a central hole of 10 mm. diameter. A steel ferrule projected outwards from this end-plate, and the narrow tube was cemented into this ferrule. A window of plate-glass covered a horizontal slot (10 mm. wide), cut out of the steel tube, and the window was fixed in position by cement. Since the window was displaced by each explosion, this steel tube was replaced, in later experiments, by a very thick-walled glass tube. One end was fitted with a steel end-plate and ferrule as described above; this end-plate was clamped to a steel annulus (which fitted over the far end of the tube) by strong bolts and nuts and the whole apparatus was supported in a wooden frame. A thin layer of cement between the metal end-plates and the glass tube rendered the apparatus air-tight.

The tubes were filled with the explosive mixture in different ways, according to their shape and construction. Where they were of small diameter, the air was displaced by a rapid stream of the explosive mixture, the cork being inserted while the gas was still passing. With wider tubes, these were tightly stoppered, rapidly evacuated to 15 mm. pressure with a Fleuss pump, and filled with gas, this operation being repeated three times in rapid succession.

*The Gases.*—The cyanogen was prepared from dried mercuric cyanide. It was mixed with dry nitrogen and oxygen obtained from cylinders of the compressed gases, and the mixture was stored in a gas holder over mercury. The hydrogen-oxygen mixtures were stored over water and passed directly into the explosion tube. The moisture present lowered the detonation rate by about 0.5 per cent., an amount well inside the experimental error. The carbon

disulphide mixtures were prepared by drawing dry oxygen through two wash-bottles containing the liquid at 18°.

The mixtures were fired by a break-spark from the secondary circuit of a Ruhmkorff coil.

In conclusion, the author desires to thank Professor H. B. Dixon for much kindly interest in the work, and Dr. O. C. de C. Ellis for considerable help with the experiments.

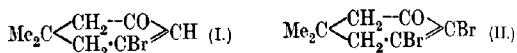
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### CCXCVI.—Action of the Chlorides of Phosphorus on Chlorodimethyldihydroresorcinol.

By LEONARD ERIC HINKEL and WILLIAM DUDLEY WILLIAMS.

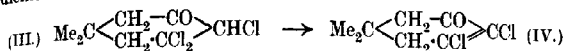
IN the course of an investigation on the action of phosphorus haloids on dimethyldihydroresorcinols (Crossley and Le Sueur, T., 1903, 83, 113) it was shown that the main products of the action of phosphorus tribromide on bromodimethyldihydroresorcinol were mono- and di-bromodimethylcyclohexenone (I and II).



For the purpose of another investigation, dichlorodimethylcyclohexenone was required, and it was hoped that it could be conveniently prepared by the action of phosphorus trichloride on chlorodimethyldihydroresorcinol, since it has been found that the action of chlorine on chlorodimethylcyclohexenone does not give rise to the dichlorodimethylcyclohexenone. (Details of this reaction will be published in a subsequent communication.) It may be at once stated that neither phosphorus trichloride nor the oxychloride has any appreciable action on chlorodimethyldihydroresorcinol, which, when heated for six hours on the water-bath with a large excess of either reagent, is in the main recovered unchanged.

It was hoped that by the regulated action of phosphorus pentachloride on chlorodimethyldihydroresorcinol it might be possible to prepare the dichlorodimethylcyclohexenone (IV). Although this result was accomplished, it was soon found that the reaction is very complicated and provides yet another example of the conversion of hydroaromatic into aromatic compounds. Several reactions apparently take place simultaneously, since unless more than two molecules of phosphorus pentachloride are employed some of the original dihydroresorcinol can always be recovered

unchanged. The primary action is the formation of a trichloro-derivative (III), which readily loses hydrogen chloride, yielding dichlorodimethylcyclohexenone (IV).



At the same time, chlorination also occurs to a small extent owing to the presence of the ketonic group (compare Armstrong and Lowry, T., 1902, **81**, 1469), yielding hydroaromatic compounds which, under the influence of phosphorus pentachloride, partly suffer rearrangement, giving rise to a monochloroxylenol, melting at 80–81°, and a xylenol, melting at 163°.

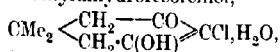
With excess of phosphorus pentachloride, a further action takes place in which the second ketonic group is attacked, yielding highly chlorinated hydroaromatic substances which partly suffer rearrangement into aromatic substances, giving rise to 3 : 4 : 5-trichloro-*o*-xylene, and 3 : 4 : 5 : 6-tetrachloro-*o*-xylene (Hinkel, T., 1920, **117**, 1300).

This rearrangement, although brought about slowly in the reaction mixture, can readily be effected by heating the hydroaromatic compounds with concentrated sulphuric acid at 120° until evolution of hydrogen chloride ceases. The aromatic compounds are obtained from the acid mixture by dilution with water and subsequent steam distillation.

Dichlorodimethylcyclohexenone is, however, not converted into an aromatic compound by this treatment, for although it is readily acted upon by concentrated sulphuric acid with evolution of hydrogen chloride, the acid mixture on dilution with water precipitates the original monochlorodimethyldihydroresorcinol, which is non-volatile in steam. This reaction definitely establishes the position of the second chlorine atom, and dichlorodimethylcyclohexenone must therefore have the constitution represented by formula IV. Although a double bond is present in the above hexenone, chlorine has no action either in hot or cold chloroform solution. With bromine, on the other hand, substitution readily takes place on heating.

#### EXPERIMENTAL.

*Action of Phosphorus Pentachloride on Chlorodimethyldihydroresorcinol.*—Chlorodimethyldihydroresorcinol,



was prepared from dichlorodimethyldihydroresorcinol by reduction with stannous chloride in warm alcohol solution as described by Vorländer (*Annalen*, 1902, **322**, 239), and dried in a steam-oven for



several hours until its melting point was  $161^{\circ}$ , corresponding with the anhydrous compound.

Twenty-seven grams of chlorodimethyldihydroresorcinol (1 mol.), 170 c.c. of dry chloroform, 50 grams of phosphorus pentachloride (1.5 mols.), and 10 c.c. of phosphorus trichloride were heated for four hours on a water-bath. The chloroform was then distilled and towards the end of the distillation a sudden reaction set in. At this stage, the distillation was stopped and the mixture poured into water and extracted three times with ether. From the aqueous layer, on keeping after removal of dissolved ether, unchanged chlorodimethyldihydroresorcinol (1.9 grams) separated in long, colourless needles. The ether layer was washed with caustic soda until the washings were alkaline (washings A), the ether was removed, and the yellow, residual liquid distilled in a vacuum, when the following fractions were collected under 13 mm. pressure:  $115-128^{\circ}$ ;  $128-132^{\circ}$ ;  $132-140^{\circ}$ ;  $140-143^{\circ}$  with decomposition. The fractions did not crystallise even after several days; they were then seeded with dichlorodimethylcyclohexenone previously isolated from the alkaline washing A (see later).

Fraction  $115-128^{\circ}$  slowly deposited crystals, especially on cooling in a freezing mixture.

Fractions  $128-132^{\circ}$  and  $132-140^{\circ}$ . Both fractions crystallised rapidly and almost completely.

Fraction  $140-143^{\circ}$ . Even after thorough cooling, only a few crystals formed.

The crystals from all the fractions were drained with suction (the mixed filtrates = B) and crystallised from light petroleum (b. p.  $40-60^{\circ}$ ), in which they are almost insoluble in the cold (yield 7.2 grams) (Found: Cl = 36.89.  $C_8H_{10}OCl_2$  requires Cl = 36.78 per cent.).

4 : 5-Dichloro-1 : 1-dimethyl- $\Delta^4$ -cyclohexen-3-one (formula IV) is very soluble in the cold in alcohol, acetone, ether, or chloroform, and crystallises from light petroleum (b. p.  $40-60^{\circ}$ ) in colourless prisms melting at  $63^{\circ}$ . It may be heated to its boiling point without decomposition. It is insoluble in cold sodium hydroxide solution and is only slightly attacked on boiling. It does not combine with chlorine either in cold or hot chloroform solution; substitution, however, takes place slowly with bromine in hot chloroform solution. One gram was heated with a few c.c. of concentrated sulphuric acid at  $120^{\circ}$ . After ten minutes, when the vigorous evolution of hydrogen chloride had subsided, the dark coloured liquid was cooled, diluted with water, and steam distilled. No volatile product was obtained, but long, needle-shaped crystals were deposited on cooling which proved to be monochlorodimethyldihydroresorcinol.

The Filtrate B was mixed with an equal volume of concentrated sulphuric acid and heated at  $120^{\circ}$  until the evolution of hydrogen chloride ceased, the dark liquid was then diluted with water and steam-distilled. The residue, on cooling, deposited long crystals of chlorodimethyldihydroresorcinol, derived from the decomposition of the dichlorodihydrocyclohexenone still remaining in the filtrate B. The ethereal extract of the steam distillate was washed with sodium hydroxide solution (washings = C), dried, and the ether evaporated, when a white residue remained which crystallised from alcohol in masses of felt-like needles. These crystals, on pressing, form a waxy mass similar to 3 : 4 : 5-trichloro-*o*-xylene (T., 1920, 117, 1299) but melting at  $107^{\circ}$ .

On repeated fractional crystallisation from ethyl acetate, a partial separation was effected yielding two substances, one melting at  $99^{\circ}$ , the other crystallising from ethyl acetate in long, glistening crystals melting at  $218^{\circ}$ . Owing to lack of material a further separation could not be effected; each fraction was therefore separately dissolved in chloroform and treated with chlorine in presence of iron filings. In each case, after removal of the chloroform, a white residue was obtained which, when recrystallised from ethyl acetate, melted at  $223^{\circ}$ , alone or mixed with 3 : 4 : 5 : 6-tetrachloroxylene (*loc. cit.*). The crystals melting at  $107^{\circ}$  were therefore a mixture of 3 : 4 : 5-tri- and 3 : 4 : 5 : 6-tetra-chloroxylene.

*Treatment of the Alkaline Washings A and C.*—The washings A were heated on a water-bath to drive off dissolved ether, then acidified with sulphuric acid and steam distilled until the distillate came over clear. The residual solution deposited crystals of chlorodimethyldihydroresorcinol on cooling.

The distillate was extracted with ether. The liquid residue, after evaporation of ether, was triturated with dilute caustic soda solution, when part of it dissolved, leaving a white solid (0.6 gram), which was filtered, dried on porous tile, and crystallised from light petroleum (b. p.  $40-60^{\circ}$ ), dichlorodimethylcyclohexenone (m. p.  $63^{\circ}$ ) being obtained. The alkaline filtrate from the hexenone was acidified with dilute sulphuric acid, extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether distilled off, when a liquid residue was obtained which slowly solidified on keeping in a cool place. This residue was found to consist of a mixture of two compounds, one soluble and the other insoluble in warm light petroleum (b. p.  $40-60^{\circ}$ ). The petroleum solution was evaporated to small bulk, when aggregates of slender crystals separated; these, after recrystallisation from light petroleum (b. p.  $40-60^{\circ}$ ), in which they are easily soluble, melted at  $80-81^{\circ}$  (Found : Cl = 23.53.  $C_8H_9OCl$  requires Cl = 22.68 per cent.).

This monochloroxylenol is very readily soluble in all the common organic solvents. It gives a benzoyl derivative melting at  $86^{\circ}$ . When treated with chlorine in light petroleum solution, it is converted into a trichloroxylenol melting at  $181^{\circ}$ .

The solid remaining after the separation of the monochloroxylenol was dissolved in hot aqueous alcohol, from which it crystallised in colourless, glistening plates melting at  $162\text{--}163^{\circ}$ ; the amount was, however, too small for further investigation.

The alkaline washings C were acidified with sulphuric acid and treated in the same manner as the alkaline filtrate from the hexenone described above, and yielded a mixture of the monochloroxylenol melting at  $81^{\circ}$  and the xylenol melting at  $162\text{--}163^{\circ}$ .

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant to one of them (L. E. H.) which has, in part, defrayed the expenses of this investigation; and also to Dr. A. W. Crossley for leaving this investigation in their hands.

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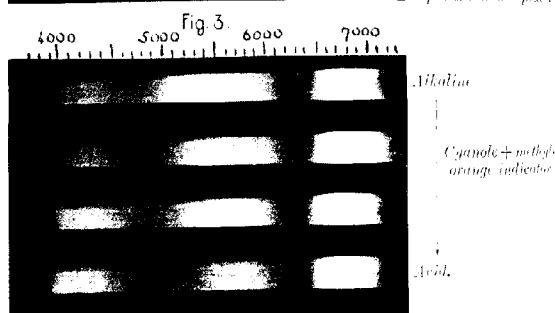
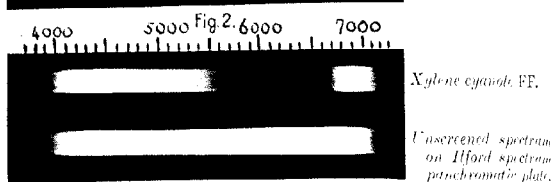
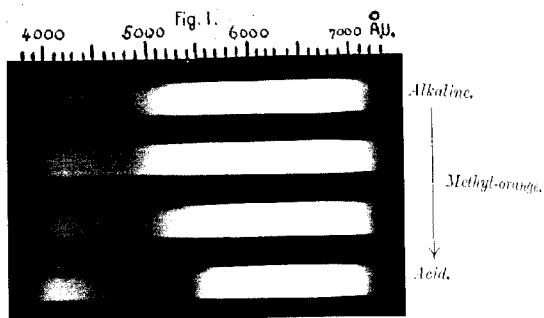
### CCXCVII.—*A Modified Methyl-orange Indicator.*

By KENNETH CLAUDE DEVEREUX HICKMAN and REGINALD PATRICK LINSTEAD.

A GREAT many substances have been employed as indicators for acid-alkali titrations, and in recent years the colour changes involved have been used for the quantitative determination of hydrogen-ion concentration. In spite of the number available, only a few indicators, such as phenolphthalein, methyl-orange, and methyl-red, are in favour for ordinary analytical work. The use of methyl-orange is almost universal, although the colour change from yellow through orange to pink is very difficult to detect in its initial stages. The object of the following work was to improve the colour change of the methyl-orange indicator without altering its chemical properties.

It is well known that the eye is most sensitive to change of hue when that change occurs to a neutral-coloured object (*Proc. Roy. Soc.*, 1900, [A], 83, 120). Thus, a red object reflecting red light diluted with 10 per cent. of white is not readily distinguishable from another red object reflecting 20 per cent. of white, provided





*In the above photographs the luminosity of the red is greatly exaggerated. The region 5000-6000 Å.U. in the top photograph (in Fig. 3) is many times brighter visually than that at 6500-7000 Å.U.*

the luminosity be the same in both cases. On the other hand, a white object appears vastly different from a nearly white object returning a 5 per cent. excess of red light. Dilute solutions of methyl-orange and phenolphthalein are good examples of this phenomenon. In acidifying methyl-orange, the change from yellow to orange is a change taking place in a previously saturated colour and is not readily noticeable. The reverse change from colourless phenolphthalein to the pink salt is immediately detectable. To improve the methyl-orange indicator, therefore, it must be modified so that the colour change is from white or neutral grey to a shade in which one or more colours preponderate.

The spectrum photograph (Fig. 1) shows the change from yellow to pink during the acidification of the dye. The absorption band shifts towards the red, obscuring the green, and permitting a little blue to pass. The eye has the difficult task of detecting a slight alteration in the length of the transmission band. Let us now suppose that an inactive substance, having a single absorption band in the yellow-orange, is added to the indicator solution. When the latter is alkaline, the colours transmitted are extreme red, green, and a trace of blue; the luminosity of the red and the blue is small compared with the green, so that the solution appears green. On acidifying, the methyl-orange band shifts into the green, reducing the luminosity of the latter until the red and blue preponderate, giving the solution a magenta colour. With the choice of a suitable screening dye there is a period during the acidification when the amounts of red, green, and blue transmitted are visually equal, so that the solution appears white, or neutral grey. The colour change is therefore, green-neutral grey-magenta, that is, from one colour, through white, to a supplementary colour; a change to which the eye is most sensitive. Furthermore, the "grey" is a definite stage and can be recognised without previous experience, and repeated from titration to titration without the use of comparison solutions.

The screening dye finally adopted was xylene cyanole FF, the mixed indicator containing one part of methyl-orange to 1.4 parts of cyanole dissolved in 500 parts of 50 per cent. alcohol. Two or three drops were sufficient for a titration, and the "grey" neutral point corresponded with a hydrogen-ion concentration of  $p_H = 3.8$ .

#### EXPERIMENTAL.

Of the many dyes examined, the following, in ascending order of usefulness, showed promise: Victoria green, patent blue A and V, filter blue-green, solid green, new solid green G, xylene

cyanole FF,\* the last-named being much better than the others.

The cyanole was found to be stable to alkalis, but decolorised by excess of mineral acid, the colour returning on dilution. In the region of the neutral point, it was insensitive to the addition of acid, and was thus suitable for the purpose.

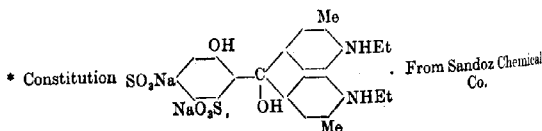
To determine the ratio of methyl-orange to xylene cyanole.

Methyl-orange. C.c. of 0.01% soln.	Cyanole. C.c. of 0.01% soln.	25 c.c. of KOH soln. re- quired of N/10-HCl (c.c.).		Contrast.
		Grey.	Pink.	
1	1.1	30.95	31.00	Fair.
1	1.2	31.05	31.10	"
1	1.3	30.90	30.95	Good.
1	1.4	30.95	31.00	Best.
1	1.5	31.00	31.10	Poor.

It will be seen that for a normal titration of 25 c.c. each of acid and alkali, 0.00010 gram of methyl-orange and 0.00014 gram of cyanole should be used. The liquid remains green to within two drops of the end-point. Another drop of acid gives a grey-green, and a further drop produces a steel-grey, showing no trace of green or pink. Further addition of acid turns the solution magenta. The question arises whether this steel-grey represents the end-point generally chosen with ordinary methyl-orange. The following comparison titrations give information on this point. As a solution of methyl-orange in pure water is yellow, the first discernible change from yellow, using a comparison solution, was assumed to be the end-point of the ordinary indicator.

Approx. strength acid and alkali.	25 C.c. of alkali required,		Excess of acid for cyanole indicator.	Mean lag in c.c.	Mean lag in c.c.
	with methyl- orange alone.	with cyanole indicator.			
N/1	No difference		Nil	Nil	Nil
N/10	30.90 c.c.	30.95 c.c.	0.05 c.c.		
"	"	"	"	0.04	0.13
"	30.80	30.85	"		
"	"	30.80	0.00		
N/50	24.4	24.5	0.10		
"	"	24.55	0.15	0.17	0.71
"	24.2	24.45	0.25		
N/100	28.4	29.10	0.70	0.78	2.8
"	28.5	29.35	0.85		

The titrations were repeated in the reverse direction, and it was



found that the lag also reversed and was slightly greater in magnitude, thus: With  $N/10$ -solutions, lag = 0.1 c.c., with  $N/50$ , lag = 0.5 c.c., with  $N/100$ , lag = 0.85 c.c. The discrepancy between the two indicators is almost negligible with  $N/10$  and stronger solutions, and is non-existent if the usual salmon-pink is chosen as the methyl-orange end-point. This is shown below:

25 C.c. of alkali of approx. strength.	C.c. of acid of nearly equivalent strength used.		
	With cyanole indicator.	First change. With methyl-orange.	Salmon-pink.
$N/10$	30.85	30.80	30.90
$N/50$	24.55	24.4	24.8
$N/100$	29.1	28.4	29.2

One of the principal uses of methyl-orange is in the estimation of carbonate and free alkali in caustic soda by the "double end-point" method, phenolphthalein being used as the first indicator. 25 C.c. of a mixture of sodium hydroxide and carbonate gave the following end-points (in c.c. of  $N/10$ -acid).

Indicator .....	Phenolphthalein.	Methyl-orange.	Methyl-orange and cyanole.
End-point .....	26.70, 26.73	29.50, 29.52	29.51, 29.53

The sensitiveness of the mixed indicator was tested for various neutralisations:

- (a) Ammonia and hydrochloric acid. Good end-point.
- (b) Sodium hydroxide and phosphoric acid. Good end-point, corresponding with formation of  $\text{NaH}_2\text{PO}_4$ .
- (c) Sodium hydroxide and acetic acid. No satisfactory end-point.

In a final experiment, one litre of distilled water containing 8 c.c. of 0.01 per cent. methyl-orange and 11.2 c.c. of 0.01 per cent. cyanole was titrated with  $N/10$ -hydrochloric acid. The colour changes were noted as follows:

C.c. of acid added.	Colour of soln.	H-ion concentration.
0.97	Slightly green.	$p_H = 3.9$
1.4	Grey.	$p_H = 3.8$
2.4	Violet.	$p_H = 3.7$

*The Use of Artificial Light during Titration.*—It was hoped that liquid or gelatin screens, coloured with cyanole or other dyes, could be used as filters for the light from electric or gas incandescent lamps to enable methyl-orange titrations to be done at night-time. It was found that whatever tint was employed, the eye adjusted itself to the general illumination, the colour of the indicator remaining substantially the same. In monochromatic light, the solution became opaque. Excellent results, equal to those obtained in daylight, were obtained by using the modified indicator in conjunction with a 100-watt gas-filled "daylight" lamp with a blue glass bulb.



*Summary.*

A method is outlined for improving the colour change of the methyl-orange indicator.

A dye is described which fulfils the necessary conditions.

The modified indicator is tested and found to be trustworthy.

A suggestion is made for procedure by artificial light.

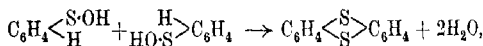
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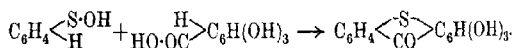
CCXCVIII.—*Derivatives of Diphenylthiolbenzene.*

By SAMUEL SMILES and HUGH GRAHAM.

IN previous communications, the characteristic reactions of *o*-dithiobenzoic acid in sulphuric acid solution have been described. These have been interpreted (T., 1911, **99**, 640) by the assumption that preliminary fission of the dithio-group occurs and that the resulting sulphenic acid undergoes condensation with other material present. Thus with benzene thioxanthone is formed (T., 1910, **97**, 1290), with hydrogen sulphide *o*-dithiobenzoyl is produced (this vol., p. 86), whilst substances containing a reactive methylene group, such as acetylacetone and ethyl acetoacetate, yield derivatives of oxythionaphthen (T., 1921, **419**, 1810). The object of the experiments now described has been to compare the behaviour of other typical aromatic disulphides with that of *o*-dithiobenzoic acid. Some evidence on this question may be collected from experiments already described in literature; for example, derivatives of thianthren are formed by heating aromatic disulphides with sulphuric acid (*Ber.*, 1909, **42**, 1170), and trihydroxythioxanthone is obtained from gallic acid and diphenyl disulphide (*Ber.*, 1911, **44**, 2146) in the same manner. In the first of these examples, the formation of the thianthren may be regarded as due to the mutual condensation of two thioaryl groups,

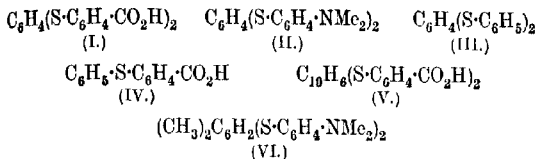


whilst in the latter an equally simple interpretation is available :



It is worth notice that the thianthren derivative arising in the former reaction is not by any means the sole product; usually, more complex substances are formed at the same time. From these instances it may be anticipated that many other disulphides are capable of condensation with aromatic nuclei. In the experiments

now described, *m*-dithiobenzoic acid and *p*-dithiodimethylaniline have been chosen as two typical disulphides; this selection has been made, partly because these substances are of widely different character, and also on account of the fact that the products which they yield are more easily obtained in the crystalline state than with other disulphides examined. Both these disulphides react very readily with benzene in presence of sulphuric acid, and in each case the chief product is a substance containing two thioaryl groups united with the benzene nucleus. The substances (I and II) are in fact derivatives of diphenylthiolbenzene (III).

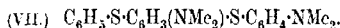


In neither instance was the simpler monosulphide of the type (IV) encountered, and this is in striking contrast with the behaviour of *o*-dithiobenzoic acid, which yields only thioxanthone under the same conditions. With the latter disulphide, only one instance has been met with in which more than one thioaryl group had condensed with the aromatic nucleus, and this was the case of naphtha-bisthioxanthone, which is formed in small quantity with naphtha-thioxanthone when *o*-thiolbenzoic acid is treated with naphthalene in sulphuric acid (T., 1910, 97, 1298). From this hydrocarbon and *m*-dithiobenzoic acid a substance of similar type (V) was obtained as the chief product. In considering the circumstances which might account for the difference in reactivity of these disulphides as compared with *o*-dithiobenzoic acid, it was thought that the presence of the ortho-substituent in the latter case might be associated with the restraining influence observed. This appeared the more probable since certain other ortho-substituted disulphides such as *o*-aniline disulphide and 1 : 4 : 1' : 4'-tetrachlorodiphenyl disulphide react only extremely slowly or not at all with benzene under comparable conditions. To submit this view to further test, the reaction of *p*-xylene with *p*-dimethylaniline disulphide was examined. Since the twofold condensation observed in the case of benzene would here lead to a substance with accumulated ortho-substituents, it was expected that either a monosulphide (type IV) would be formed or that reaction would not occur. It was found, on the other hand, that rapid condensation took place with formation of the bis-sulphide (VI). Under the same conditions, *o*-dithiobenzoic acid yields (T., 1911, 99, 1355) 1 : 4-dimethylthioxanthone.

This example is sufficient to show that ortho-substitution is not the sole factor which is concerned in the more restrained activity of the *o*-dithio-acid. On reviewing the situation, it seems more probable that the difference is due to the formation at the first stage in the condensation of a stable cyclic system; thioxanthone does not readily yield the bithioxanthone with excess of the dithio-acid, and it is the sole product when the acid reacts with benzene under usual conditions. The same circumstances obtain in the intramolecular condensation of a simple aromatic disulphide such as the *p*-tolyl derivative, which furnishes dimethylthianthren.

Turning to the behaviour of *m*-dithiobenzoic acid and of *p*-dithio-dimethylaniline with substances containing reactive methylene groups, it is remarkable that in neither case has any reaction yet been observed similar to those which take place so readily with *o*-dithiobenzoic acid. In this respect the latter substance appears quite exceptional.

The following remarks on the structures of the substances described in the following pages are necessary. It is clear that they do not contain the dithio-arrangement found in the disulphides from which they are prepared, for they are not attacked by reducing agents with formation of mercaptans. The question then arises as to the order in which the thioaryl groups and the nucleus of the hydrocarbon taken are associated. For example, in the case of the substance obtained from benzene and dithiodimethylaniline, there would be the alternative arrangements II and VII :



The latter implies that the disulphide is capable of undergoing intramolecular condensation under the conditions chosen. Experiments have shown that this is not the case; *p*-dithiodimethylaniline may be recovered unchanged after its solution in sulphuric acid has been kept at 20°, but reaction at once begins when the hydrocarbon is added. The same remarks apply to the case of *m*-dithiobenzoic acid. Hence the alternative structure (II) must be accepted. With regard to the orientation of the thioaryl groups in the hydrocarbon nucleus, nothing can at present be said, except in the case of *p*-xylene, where the ortho-situation with respect to the methyl groups is undoubted.

#### EXPERIMENTAL.

*Benzenedi-m-thiobenzoic Acid*,  $C_6H_4(S \cdot C_6H_4 \cdot CO_2H)_2$ .—A mixture of 15 grams of *m*-dithiobenzoic acid and 150 c.c. of sulphuric acid was shaken with 10 c.c. of benzene at the atmospheric temperature. Two further additions of the same amount of benzene were made at

intervals of half an hour. The interaction proceeded with evolution of sulphur dioxide, whilst the reacting mixture assumed a deep green colour. After being shaken for three hours, the liquid was kept overnight, when a considerable portion of the crystalline product separated. The mass was then poured over crushed ice, and the solid thus obtained was dissolved in aqueous sodium hydroxide and solid sodium hydroxide added, when crystals of the sodium salt of the required acid separated. A sample of this material was recrystallised from hot water.

*Sodium benzenedi-m-thiobenzoate* was then obtained in broad, colourless prisms which are moderately soluble in cold water. This salt contained water of crystallisation, but the amount retained by an air-dried sample varied and was not in any definite molecular proportion (Found:  $\text{H}_2\text{O} = 15.5\text{--}16.6$ . Calc.,  $2\text{H}_2\text{O} = 12.5$ ;  $3\text{H}_2\text{O} = 17.6$  per cent.). The water present was removed by heating the substance at  $130^\circ$ ; the anhydrous material then obtained ( $\text{Na} = 10.87$ ; calc.,  $\text{Na} = 10.79$  per cent.) being hygroscopic. The chief portion of the crude sodium salt was treated with dilute sulphuric acid and the amorphous material liberated was submitted to further purification. It was first treated with ether in an extraction apparatus to remove inorganic matter. The required acid separated from the ether in the crystalline state, but it was finally recrystallised several times from a hot mixture of alcohol and water. *Benzenedi-m-thiobenzoic acid* forms a colourless microcrystalline powder which is very sparingly soluble in ether and moderately soluble in boiling alcohol or acetone; when immersed in a bath at  $280^\circ$ , it subsequently melts and slightly decomposes at  $302\text{--}303^\circ$  (Found:  $\text{C} = 62.7$ ;  $\text{H} = 3.9$ ;  $\text{S} = 16.9$ .  $\text{C}_{20}\text{H}_{14}\text{O}_4\text{S}_2$  requires  $\text{C} = 62.78$ ;  $\text{H} = 3.7$ ;  $\text{S} = 16.8$  per cent.). When pure, the substance yields a colourless solution with sulphuric acid, the green colour which appears during the preparation being apparently due to an oxidation product. The yield of the crude material is about 80 per cent. of theory, but the treatment necessary to remove the impurity greatly diminishes this amount.

*Naphthalenedi-m-thiobenzoic Acid*,  $\text{C}_{10}\text{H}_6(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ .—A mixture of *m*-dithiobenzoic acid and sulphuric acid was treated with a solution of naphthalene in light petroleum as in the case of benzene; the subsequent treatment was similar, but to purify the product it was found necessary to repeat the precipitation of the sodium salt with alkali several times. The acid finally liberated from this was recrystallised from a mixture of alcohol and water. Prepared in this manner, *naphthalenedi-m-thiobenzoic acid* forms small, yellow needles which melt and decompose at  $256\text{--}258^\circ$  and are sparingly soluble in the common organic solvents (Found:  $\text{C} = 66.25$ ;  $\text{H} = 3.9$ ;

$S = 14.5$ ;  $M$ , in boiling nitrobenzene,  $= 449$ .  $C_{24}H_{16}O_4S_2$  requires  $C = 66.6$ ;  $H = 3.7$ ;  $S = 14.8$  per cent.;  $M = 432$ ).

*Benzenedi-p-thiodimethylaniline*,  $C_6H_4(S-C_6H_4-NMe_2)_2$ .—A solution of *p*-dithiodimethylaniline in sulphuric acid was shaken with benzene at the atmospheric temperature, further small quantities of benzene being added until the evolution of sulphur dioxide had ceased. The liquid obtained by pouring the green reaction mixture over crushed ice was neutralised with sodium carbonate, the precipitated base collected in chloroform, the solvent removed, and the residue treated with a little acetone to remove coloured impurities and then recrystallised from acetone. *Benzenedi-p-thiodimethylaniline* forms colourless, broad needles which melt at  $171-172^\circ$  (Found:  $C = 69.4$ ;  $H = 6.5$ ;  $S = 17.0$ ;  $M = 402$ .  $C_{22}H_{24}N_2S_2$  requires  $C = 69.4$ ;  $H = 6.3$ ;  $S = 16.8$  per cent.;  $M = 380$ ). It is worth notice that the condensation of this disulphide with phenol under the same conditions as those now described has been previously examined (T., 1911, 99, 648). The product then isolated was the substance  $HO-C_6H_3(S-C_6H_4-NMe_2)_2$ . It is evident that the course of the reaction is similar in the two cases.

*p-Xylenedi-p-thiodimethylaniline*,  $(CH_3)_2C_6H_2(S-C_6H_4-NMe_2)_2$ .—Dimethylaniline *p*-disulphide was treated with *p*-xylene in sulphuric acid as described in the foregoing case. The solution obtained by pouring the reaction mixture over ice was extensively diluted with water, when the required product was precipitated. This was collected and recrystallised first from alcohol and then from acetone, when *p-xylenedi-p-thiodimethylaniline* was obtained in colourless needles. When rapidly heated, these melted at  $232-233^\circ$  (Found:  $S = 16.2$ ;  $N = 7.1$ ;  $M = 403$ .  $C_{22}H_{28}N_2S_2$  requires  $S = 15.8$ ;  $N = 6.8$  per cent.;  $M = 408$ ). This substance is less stable than the corresponding derivative obtained from benzene; for example, the solution in boiling acetic acid rapidly assumes a violet colour, apparently owing to oxidation, but no definite product could be isolated.

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## CCXCIX.—Chlorination of Benzoyl Chloride. Part I.

By EDWARD HOPE and GEORGE CLIFFORD RILEY.

AMONG the problems concerning the influence of the character of an atom or group, substituted in the benzene ring, on the position taken up by another atom or group entering the ring,

the interesting case where the group  $\text{-COCl}$  is present does not appear to have been studied. Since benzoyl chloride is a liquid, it seemed highly probable that, of the simple substituting reactions, direct halogenation would be possible, and it was decided to investigate this. In the literature, there are only two references to the action of substituting agents on benzoyl chloride, namely, Karslake and Huston (*J. Amer. Chem. Soc.*, 1909, **31**, 479) and Bornwater and Holleman (*Rec. trav. chim.*, 1912, **31**, 221). The first-mentioned authors found that the action of nitric acid or nitric anhydride on a solution of benzoyl chloride in acetic anhydride gave only nitro- and acetyl derivatives of benzoic acid. Hydrolysis of the chloride was supposed to precede any other action. The work of the latter authors was mainly devoted to the chlorination of benzoic acid. They mention, however, the action of liquid chlorine on benzoyl chloride in sunlight. This results, according to them, in the formation of an additive product. The reaction is described as taking place very readily and the main product is a hexachloro-additive product of benzoyl chloride, boiling at  $171\text{--}172^\circ/0.5\text{ mm.}$ , accompanied by traces of chlorine substitution products and hexachlorobenzene.

In some preliminary experiments, dry chlorine was passed into benzoyl chloride in the absence of a catalyst, and the main results indicated by Bornwater and Holleman were obtained. Contrary, however, to their experience, we found, on allowing the solution of chlorine in benzoyl chloride to stand in bright daylight and in direct sunlight, no rapid disappearance of the yellow colour of the chlorine to occur. Even after many hours, chlorine persisted. An experiment, similar in every way except that a small amount of anhydrous ferric chloride was added, gave a totally different result. The chlorine was rapidly absorbed at the ordinary temperature, much heat developed, and hydrochloric acid fumes evolved. When an increase of weight corresponding with the substitution of one atom of chlorine for hydrogen had occurred, the liquid was shown to consist mainly of monochlorobenzoyl chlorides (mainly meta-) along with small amounts of unchanged benzoyl chloride and of dichlorobenzoyl chlorides. The estimation of the amount of monochloro-derivatives and their isolation (which was one of the original objects of this work) are obviously much simpler matters in the case of the chlorides than in the case of the acids, for the process of fractional distillation ensures the removal of the unchanged benzoyl chloride and of practically all the dichlorobenzoyl chlorides.

The estimation of the amounts of the individuals in the product was accomplished by fractionally distilling the chlorination product

several times at low pressure, collecting a number of fractions boiling between definite temperatures, and estimating with the aid of melting-point diagrams the amounts of benzoic and individual chlorobenzoic acids in the mixtures from the hydrolysis of each of the fractions. The exact procedure is described in the experimental part, p. 2516.

When the chlorination was conducted at 35° and the increase in weight corresponded with the entry of one chlorine atom (ferric chloride being the catalyst), the results obtained in the analysis of that portion of the product which boiled below 121°/12 mm. indicated that, of the original benzoyl chloride, 13.5 per cent. was unchanged, 76.0 per cent. was converted into monochlorobenzoyl chlorides, and 5.0 per cent. was converted into dichlorobenzoyl chlorides.

The remaining 5.5 per cent. of benzoyl chloride was converted into tarry material (containing iron derivatives of benzoic and chlorobenzoic acids) and probably also to some extent into tri- and poly-derivatives of benzoyl chloride.

The monochlorobenzoyl chlorides consisted of the three isomerides in the following proportions : meta-, 83.5 per cent. ; ortho-, 14.5 per cent. ; para-, 2.0 per cent.

The most closely allied substitution reaction the results of which it is of interest to compare with the above is the chlorination of benzoic acid, but in spite of a good deal of work on the subject no results of a quantitative nature have been obtained. A summary of these results is given by Holleman ("Die direkte Einführung von Substituenten in den Benzolkern," 1910, p. 114) and the general conclusion formed is that chlorination of benzoic acid in acid solution favours the production of the meta-substituted acid; in neutral or basic solution, the ortho- and para-acids are the main constituents. Later, Bornwater (*Rec. trav. chim.*, 1912, **31**, 221) found great difficulty in analysing a mixture of benzoic, monochlorobenzoic, and dichlorobenzoic acids formed by the chlorination of benzoic acid with liquid chlorine. He roughly estimated the amount of *m*-chlorobenzoic acid formed at 70 per cent., and did not isolate any ortho- or para-substituted acids.

The only allied reaction in which a really quantitative analysis of the products formed has been carried out is the nitration of benzoic acid. Holleman (*Rec. trav. chim.*, 1899, **18**, 267) gives the following as the percentage composition of the mononitro-substitution product in the case of nitration at 30° : meta-, 76.5 per cent. ; ortho-, 22.3 per cent. ; para-, 1.2 per cent.

These proportions are of the same order as those obtained in the present investigation. •

A number of methods were investigated with the view of finding

a process of separation of the monochlorobenzoic acids from one another or at any rate a separation of the main product—meta—from the others. Only one of the methods tried, however, gave a reasonably good result, namely, fractional crystallisation of the mixed barium salts from water, based on the comparatively small solubility of the salt of the *m*-isomeric. In this way, it was possible to separate a large proportion of almost pure *m*-chlorobenzoic acid from a mixture. Also, by examination of the composition of the other fractions, confirmation of the analytical results given by the purely physical method was obtained, as well as direct evidence of the presence of the *o*- and *p*-chloro-acids.

## EXPERIMENTAL.

The benzoyl chloride was prepared from pure benzoic acid and phosphorus pentachloride in the usual manner, purified by distillation, and finally carefully fractionally distilled, the fraction boiling at 196.8–197°/764 mm. being collected. The three monochlorobenzoyl chlorides were also similarly prepared from the pure chlorobenzoic acids, and values for the boiling points of these, and of the benzoyl chloride, determined at various pressures,\* as follows :

*Benzoyl chloride.*

Pressure .....	9	10.5	13	15.5	19.5	25	28	35.5 mm.
Temperature .....	71°	75°	79°	82.5°	87°	92.5°	94.5°	100.5°.

*o*-Chlorobenzoyl chloride.†

Pressure .....	11	12	12.75	14.5	19.75	26.5 mm.
Temperature .....	101.5°	103.5°	105°	108°	114.5°	122°.

*m*-Chlorobenzoyl chloride.

Pressure .....	10	12.5	15	19	21	26 mm.
Temperature .....	94.5°	99.5°	103.5°	109.5°	112°	117.5°.

*p*-Chlorobenzoyl chloride.†

Pressure .....	10.5	11.5	15	18.5	27.5 mm.
Temperature .....	97.5°	99°	104.5°	109°	119°.

\* These determinations, and the fractional distillation of reaction mixtures obtained in the chlorination experiments, were carried out in flasks which had columns of the pear-shaped bulb type sealed directly on to the neck, and a side tube entering below the column, by which they could be emptied. These were necessary because the hot vapour of all these chlorides attacks cork or rubber extremely vigorously. Precautions were always taken against the entrance of moisture from pump or air.

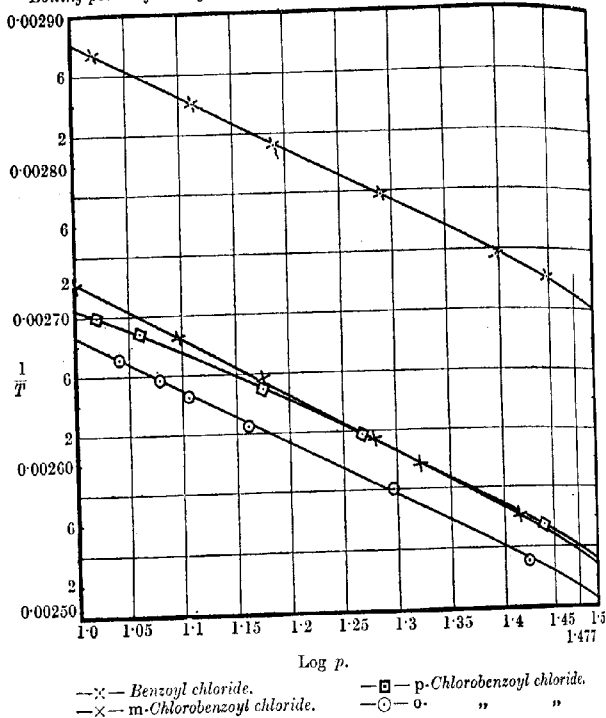
† Fritsch (*Ber.*, 1896, 29, 2299) gives the value 110°/15 mm. for the ortho-, and Montagne (*Rec. trav. chim.* 1900, 19, 46) gives the value 111.5°/18 mm. for the para-compound.



These results are plotted on the accompanying curve (Fig. 1), in which values of  $\log p$  and  $1/T$  are taken as co-ordinates, giving practically straight lines ( $p$  = pressure in mm. and  $T$  = absolute temperature).

Fig. 1.

*Boiling points of benzoyl chloride and o-, m-, and p-chlorobenzoyl chlorides.*



Values of the boiling points taken at three definite pressures from these curves for comparison are as follow :

Pressure.	Boiling point.			
	Bz.	Ortho.	Meta.	Para.
10 mm.	74.0°	90.4°	94.4°	96.5°
20 mm.	87.5	114.9	110.5	110.7
30 mm.	96.1	124.7	121.1	120.5

The values of  $A$  and  $B$  in the equation  $\log p = A - B/T$  for each compound are thus

	A.	B.
Benzoyl chloride .....	8.95	2758
<i>o</i> -Chloro- " .....	8.49	2790
<i>m</i> -Chloro- " .....	8.02	2579
<i>p</i> -Chloro- " .....	8.89	2909

The small difference in the boiling points of the three chloro-isomerides indicates that they behave as normal benzene derivatives (Sidgwick, T., 1920, 117, 392). It is, however, remarkable that the ortho-compound should have the highest boiling point. The same occurs in the case of the phthalyl dichlorides (*o*-, 281°; *m*-, 276°; *p*-, 259°).

*Action of Chlorine on Benzoyl Chloride without Carrier.*

A steady stream of thoroughly dried chlorine was bubbled through benzoyl chloride (44 grams) contained in a small flask protected from the air, and in sunlight. The chlorine formed a deep yellow solution in the liquid, and the temperature rose rather rapidly from 15° to 22°, then fell slowly to 18°, at which it remained constant. The weight of the mixture only rose extremely slowly, with a slight evolution of hydrogen chloride gas. When the increase in weight reached 6 grams, the whole was left for forty-eight hours (in sunlight during the daytime), but the yellow colour did not perceptibly diminish. Chlorine was again passed until the total increase in weight reached 12 grams (theoretical increase for one chlorine atom = 11 grams), and the whole fractionally distilled at 20 mm. pressure. The chlorine boiled off, leaving a colourless liquid, of which 38 grams passed over between 88—96°, and the remainder between 203—210°; the latter being a colourless, very viscous liquid. The first fraction was shown to be nearly pure benzoyl chloride, and so only one-sixth of the original chloride had been used up, to form a compound probably identical with Bornwater's benzoyl chloride hexachloride.

*Action of Chlorine on Benzoyl Chloride in the Presence of Anhydrous Ferric Chloride.*

Preliminary experiments, similar to the last, but with the addition of a small quantity of anhydrous ferric chloride to the benzoyl chloride, showed that the chlorine was much more rapidly absorbed, with evolution of heat and hydrogen chloride, and that the main product of the reaction was *m*-chlorobenzoyl chloride.

A regulated chlorination for analysis of the products was carried out as follows.

Anhydrous ferric chloride (7 grams) was added to benzoyl chloride (429 grams) in a round flask (600 c.c. capacity), forming a deep

yellowish-red solution, but leaving some of the ferric chloride undissolved. The flask was immersed in a water-bath kept at constant temperature (35°), and tightly fitted with a cork carrying an inlet tube for the chlorine dipping well under the liquid, a sealed stirrer,\* and a vertical air-condenser for the exit of the gases. From the top of this condenser a tube led down and dipped under the surface of strong sulphuric acid in a small flask, thus indicating the rate of passage of the gas, and preventing the entrance of moisture. The flask and fittings could be removed bodily, and the inlet tube and top of the air-condenser closed by rubber caps, for weighing.

The chlorine used was from a cylinder, and was dried thoroughly by strong sulphuric acid before passing into the benzoyl chloride.

The apparatus was shaded from strong light, and, with rapid stirring, chlorine was passed through in a steady stream, the flask being weighed at intervals until the increase in weight was the theoretical for the substitution of one atom of chlorine (106 grams), the final weight being taken after prolonged stirring and standing over-night, as follows :

Time from commencement	2	3½	4½	5½	5½ hours.
Increase in weight.....	21	51	73	100	106 grams.

Thus the final total weight of liquid was 542 grams. This was of a very deep red colour, and there was no undissolved solid.

*Distillation of the Reaction Mixture.*—530.2 Grams of the liquid were weighed into a distilling flask, heated at about 100° at 10 mm. pressure, until it was on the point of distilling, reweighed, and finally distilled at this pressure until the thermometer reading was 98°.

The loss in weight before distillation was 2.5 grams.

There distilled over between 83—98° 401.1 grams.

The residual liquid in the flask was diluted with pure dry light petroleum (500 c.c. of the fraction boiling at 60—75°, in which these chlorides are readily soluble), and kept for some hours. A quantity of a deep red oil was deposited, and the solution, which still had a slight yellow colour, was poured off into a fractionating flask, the solvent distilled off, and the remainder fractionally distilled at 12 mm. pressure. The above 401.1 grams fraction was similarly

\* Rapid agitation of the mixture was found to be essential, otherwise the hydrogen chloride formed did not seem to be readily evolved, and this considerably slowed down the reaction, and also made the determination of the increase in weight very difficult, owing to the considerable weight of dissolved gas. With stirring, the correct weight of the mixture could be taken almost immediately after stopping the passage of the chlorine.

fractionally distilled, and the corresponding fractions combined, giving

78—90°	34 grams.	101—104°	108.5 grams.
90—97°	70 "	104—110°	62.4 "
97—101°	176.8 "	Residue *	47.2 "
		Total .....	498.9 "

\* This residue was still deeply coloured, so it was treated with the light petroleum recovered from the first precipitation, allowed to stand, the petroleum poured off, and distilled, and the residue from this distillation added at the suitable point to the next fractional distillation of the main bulk.

This procedure was adopted to prevent the loss and decomposition which had been found to take place on distilling the highest boiling fractions from the mixture of ferric compounds and tar present.

It was found to be inadvisable to attempt the precipitation at an earlier stage, before a preliminary distillation, as too large a volume of light petroleum was required for complete separation.

The total red oil that separated was dried at 100°, and weighed 25.7 grams.

The above fractions were fractionally redistilled a further five times at 12 mm. pressure, giving as final fractions

75—80°	42.8 grams.	103—105°	10.7 grams.
80—85°	7.0	105—110°	9.3
85—90°	7.1	110—115°	5.3
90—98°	35.2	115—120°	14.9
98—99°	196.8	120—121°	27.3
99—100°	70.0	Residue	16.9
100—101°	19.2		
101—103°	20.5	Total	483.0
	39.7		

As the original weight of volatile liquid undergoing distillation was  $530.2 - (2.5 + 25.7) = 502$  grams, the total loss of liquid during the whole of the distillations  $= 502 - 483 = 19$  grams, that is, the average loss per distillation  $= 0.54$  per cent. of the liquid distilled. It cannot introduce an appreciable error to assume that in each distillation this small loss was distributed evenly over the various fractions, and a correction for this loss is made in the final calculation of the analysis of the mixture.

*Hydrolysis of the Fractions to Corresponding Acid Mixtures.*—This was found to be best effected by boiling with water. A weighed amount of any particular chloride fraction was boiled under reflux with three or four times its weight of water, the chloride layer becoming opaque and milky, and finally clear again. With mixtures containing the *m*-chloro-compound as main constituent, crystals of the acid grew in star-shaped clusters of long needles on the sides of the flask. With mixtures of low melting point, the lower layer

remained liquid, and the completion of the hydrolysis was denoted by a characteristic cloudy appearance of the boiling, upper, aqueous layer. This generally took place at about three-quarters of an hour from the commencement of boiling.

With mixtures of higher boiling point, at the end of half an hour from the commencement, the lower layer completely solidified, with evolution of heat. The solid cake was broken up and the boiling continued for a further half hour. The condenser was washed down with water, and the contents of the flask were cooled to  $0^{\circ}$ , filtered, and washed with a little cold water. The solid was dried at  $100^{\circ}$ , ground to a powder when nearly dry, and finally dried until free from moisture and acid.\*

The amount left in solution in the water was small, but was extracted by pure ether, and taken into account in the analysis (as it was usually of different composition from the main bulk).

*Example.*—13.19 Grams of 100–103° fraction gave

11.51 grams of acid melting at  $129$ – $136^{\circ}$ , the m. p. being raised by the addition of *m*-chlorobenzoic acid.

0.17 gram extracted from aqueous solution; melting at  $127$ – $127.8^{\circ}$ , the m. p. being raised by the addition of *o*-chlorobenzoic acid.

11.68

Theoretical yield, calculated on composition later found by analysis = 11.8 grams.

*Method of Analysis of the Acid Mixtures.*—The estimation of the proportions in which the different acids were present in the mixtures after hydrolysis was carried out by means of a series of solidification-point determinations.

Briefly, in the case of any particular mixture, the method was to determine two types of solidification point :

(a) The initial solidification temperature of the mixture. From the value of this, the proportion of the main constituent could be deduced from the curves given by Bornwater and Holleman (*Rec. trav. chim.*, 1912, **31**, 242) for binary mixtures of these acids.

(b) A eutectic temperature. For this determination, a suitable calculated addition of one of the pure acids was made, such as would bring the relative proportions of the latter and the original main constituent approximately to their true eutectic proportions, irrespective of the other acid or acids present. From the value of the eutectic temperature of this mixture, the proportion of the

\* These dry powders were extremely easily electrified by the slightest friction, with consequent scattering.

remaining constituent could be deduced from curves obtained by the authors for the effect of known additions to pure eutectic mixtures.

*Discussion of Method.*—(a) T. van der Linden (*J. Chim. Phys.*, 1912, 10, 465) points out that in the case of any mixture of benzoic acid with the monochlorobenzoic acids, where the initial solidification temperature falls on the benzoic side of the eutectic, a determination of this solidification temperature affords an accurate means of estimating the amount of benzoic acid in the mixture, irrespective of the number or relative amounts of the chloro-acids present.

This follows from the fact that the initial solidification temperature of benzoic acid is lowered to exactly the same extent by the same weight of either of the three monochlorobenzoic acids (Bornwater and Holleman, *loc. cit.*).

The same holds true for the addition to *m*-chlorobenzoic acid, *o*-chlorobenzoic acid, or *p*-chlorobenzoic acid, respectively, of either of the other two or benzoic acid itself (although not in every case quite so accurately). Thus it can be taken as very nearly correct that from the initial solidification point of any mixture of these four acids, can be deduced the proportion of the main constituent *A* (that is, the one which first separates at this point). This is especially correct when one of the remaining acids (*B*) forms a large proportion of the remainder. The value required for the proportion of *A* is then read from the curve for mixtures of *A* and *B*.

The determinations of solidification points were carried out in a similar manner to that described by Bornwater (*loc. cit.*). The tube containing the mixture, thermometer, and glass stirrer was supported centrally inside a slightly wider tube, and the whole immersed in a stirred glycerol bath, illuminated from behind, and kept at a temperature a few degrees above the melting point of the mixture until the latter was totally melted. The temperature of the outer bath was then allowed to fall very slowly, so that it was never more than two or three degrees below the temperature of the mixture. The initial solidification temperature was taken as that temperature at which crystals appeared in the liquid mixture and just perceptibly increased in amount, after seeding with small amounts of solid from cooler portions of the thermometer.

Eutectic temperatures were determined in a similar apparatus. In this case, after a small amount of solid had separated, the temperature of the mixture stopped falling and remained steady for some time. This value was taken as the eutectic temperature.

(b) Van der Linden (*loc. cit.*, p. 460) describes the use of eutectic

determinations for the analysis of ternary and quaternary mixtures. The way, however, in which he determines these points, by cooling a mixture which has a composition very different from that of the eutectic mixture, presents great difficulties, as he admits. In experiments carried out in this way, a large amount of solid separates before the eutectic point is reached, and this makes an accurate determination difficult and prohibits its use where there is any mixed crystal formation (this takes place to a slight extent with *m*- and *o*-chlorobenzoic acids). It is also essential to know which eutectic mixture separates at the point determined.

These difficulties were overcome, in the case of the mixtures obtained in the present investigation, by making a calculated addition of one of the pure acids such as would convert the relative proportions of the two main constituents into the proportions of their eutectic mixture. On determining this eutectic temperature, a very small amount of solid separates before the required temperature is reached, and the above difficulties are obviated. When a third acid is present, the temperature found is lower than that of the true eutectic of the pure substances, by a difference proportional to the amount of the third present. This amount can be deduced from a curve plotted from the results of determinations on known mixtures. Two such curves were determined as follows :

(1) A eutectic mixture of pure benzoic (64 per cent.) and *m*-chlorobenzoic (36 per cent.) acids was made up, and values obtained for the lowering of the eutectic temperature brought about by the addition of varying weighed amounts of pure *o*-chlorobenzoic acid, as far as the ternary eutectic point (Table I and Fig. 2). The amounts of *o*-chlorobenzoic acid are given as percentages on the total weight of *o*-chlorobenzoic acid plus benzoic acid, as this is the most convenient form for calculating from the results of determinations on unknown mixtures. The small amount of solid separating out before the eutectic temperature was reached was shown in each case to be *m*-chlorobenzoic acid, as the addition of a small amount of the latter raised the temperature at which solid first separated, but did not affect the temperature of the eutectic point.

(2) Similar values were obtained for the case of the addition of pure *p*-chlorobenzoic acid to a eutectic mixture of *o*-chlorobenzoic acid (53 per cent.) and *m*-chlorobenzoic acid (47 per cent.), as far as was found necessary for the determination of the mixtures encountered (Table II).

Thus the method of analysis of a mixture containing, say, *m*-chlorobenzoic acid as main constituent, together with benzoic

TABLE I.

Addition of *o*-chlorobenzoic acid to the eutectic mixture of benzoic and *m*-chlorobenzoic acids (Bz, 64 per cent.; *m*-, 36 per cent.).

<i>o</i> -Chlorobenzoic acid per cent., calculated on total weight of benzoic plus <i>o</i> -chlorobenzoic acids.	Solidification temperatures.		
	Initial.	Binary eutectic.	Ternary eutectic.
0	95.7°	95.4°	
3.4		93.9	
6.9		92.5	
12.2		89.7	
16.3		87.6	
19.1		86.2	
21.8	86.3	85.0	} varied between 81.6—82.0°.
24.4	85.1	83.6	
25.5	84.1	82.9	
26.8	83.8	82.5	
28.0	83.7	82.3	
29.3	85.2	83.2	
32.0	86.8	85.2	

TABLE II.

Addition of *p*-chlorobenzoic acid to the eutectic mixture of *o*- and *m*-chlorobenzoic acids (*o*-, 53 per cent.; *m*-, 47 per cent.).

<i>p</i> -Chlorobenzoic acid per cent., calculated on total weight of <i>o</i> - plus <i>p</i> -chlorobenzoic acids.	Solidification temperatures.	
	Initial.	Binary eutectic.
0	111.2°	110.6°
2.9	110.5	109.8
6.0	109.5	108.7

acid, and *o*- or *p*-chlorobenzoic acid in small quantity, was as follows.

The proportion of *m*-chlorobenzoic acid was found by the initial solidification temperature of the original mixture.

Until the proportions of the remaining constituents were known, the remainder was taken as being wholly benzoic acid, and to a weighed portion of the mixture the calculated quantity of benzoic acid was added that would convert the percentage of *m*-chlorobenzoic acid to 36 per cent. of the resulting mixture, and the eutectic temperature determined. If this were 95.4°, the absence of *o*- or *p*-chlorobenzoic acid was thus proved. If it had a lower value, from the curve (Fig. 2) the proportion of the ortho-acid in the total weight of benzoic acid plus ortho-acid (which = 64 per cent. of the whole mixture) was found, and so the percentage in the original mixture calculated. If this amount were considerable, the eutectic temperature was redetermined after a corrected addition of benzoic acid to bring the proportion of meta-acid: benzoic acid = 36:64, and the final calculation was based on this value.



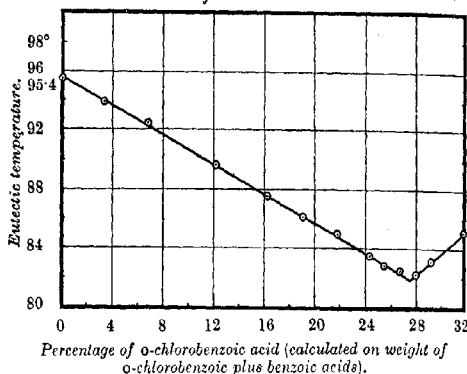
Another addition, of sufficient *o*-chlorobenzoic acid to form practically the ternary eutectic mixture (of *m*- and *o*-chlorobenzoic and benzoic acids) was then made, and this point determined. The value proved that the third substance present was the *o*-chloro-acid, or any lowering indicated the presence of the *p*-chloro-acid.

In mixtures where benzoic acid was absent, this was proved by a value being obtained for the percentage of *o*-chlorobenzoic plus *p*-chlorobenzoic acids in the original mixture which was identical with 100 minus the percentage of the *m*-chloro-acid.

In these cases, the amount of the *o*-chloro-acid, and the absence, or amount if present, of the *p*-chloro-acid, were determined in a similar manner by use of the eutectic point of the *m*-chloro- and

FIG. 2.

Curve showing effect on eutectic temperature of addition of *o*-chlorobenzoic acid to eutectic mixture of *m*-chlorobenzoic and benzoic acids.



*o*-chloro-acids. To the original mixture sufficient *o*-chloro-acid was added to reduce the percentage of the *m*-chloro-acid to 47 per cent. of the resulting mixture (the value for the meta-ortho eutectic), and the eutectic temperature determined. This value, by means of Table II, was used to calculate, in a similar manner, the amount of *p*-chlorobenzoic acid in the original mixture.

Mixtures containing *m*-chlorobenzoic acid admixed with small quantities of all three, benzoic, *o*-chloro-, and *p*-chlorobenzoic acids, were not encountered in this investigation, but such mixtures could be estimated by a combination of the above methods, first obtaining the percentage of *o*-chloro- plus *p*-chloro-acids from a determination of the *m*-chlorobenzoic-benzoic eutectic, and then the percentage of benzoic plus *p*-chlorobenzoic acid from a determination of the meta-ortho eutectic.

*Example:*

25.14 Grams of the fraction boiling at 98—99°/12 mm. on hydrolysis gave

21.7 grams of main product (a) and 0.42 gram extracted from the aqueous solution (b).

(a) *Main product*.—The initial solidification temperature was 149.2°, raised by addition of *m*-chlorobenzoic acid, indicating 92 per cent. of *m*-chlorobenzoic acid.

0.2616 Gram plus 0.3865 gram of benzoic acid gave a eutectic temperature of 93.2°.

Therefore, in the resulting mixture,

ortho-acid (plus any para-acid) : benzoic acid  
= 5.2 : 94.8 (by Table I),

but the amount of meta-acid =  $0.92 \times 0.2616 = 0.2406$  gram.

Therefore the amount of ortho- (plus para-) acid

=  $0.052 \times (0.6481 - 0.2406)$   
= 0.0212 gram,

and as  $0.2616 - 0.2406 = 0.0210$  „

this proves the total absence of benzoic acid in the original mixture.

0.6565 Gram of the resulting mixture plus 0.1285 gram of *o*-chlorobenzoic acid gave the eutectic temperature 81.5° (the initial solidification temperature being 83.6°), indicating the presence of some para-acid.

0.297 Gram of the original mixture plus 0.238 gram of ortho-acid (so that meta-acid = 0.2732 gram, remainder = 0.3118 gram) gave a eutectic temperature of 109.8°.

Therefore, in this mixture, para-acid : ortho-acid

= 2.9 : 97.1 (by Table II),

and the para-acid in the original mixture

=  $0.029 \times 0.3118 = 0.009$  gram  
= 3 per cent. of mixture

and the ortho-acid

= 5 „ „

(b) *Ether extract*.—The initial solidification temperature was 124°, raised by the addition of *o*-chlorobenzoic acid, indicating 74.5 per cent. of *o*-chlorobenzoic acid.

0.343 Gram plus 0.15 gram of *m*-chlorobenzoic acid gave a eutectic temperature of 110.4°, indicating less than 1 per cent. of an acid other than the ortho- and meta-acids, which is negligible on the total fraction.

Thus the combined analysis for the total fraction is

<i>m</i> -chlorobenzoic acid	90.7 per cent.
<i>o</i> -chlorobenzoic acid	6.3 „
<i>p</i> -chlorobenzoic acid	3.0 „

The 120–121° fraction on hydrolysis was shown to consist solely of dichloro-compounds. Repeated crystallisation of the acid mixture isolated a pure specimen of 2:5-dichlorobenzoic acid. A small percentage of these dichloro-compounds was also found to remain in the next lower fraction, 105–120°.

The higher volatile residues were not examined, but it is extremely probable that these contained tri- and more highly chlorinated compounds.

The insoluble residue from light petroleum was boiled with 400 c.c. of dilute hydrochloric acid, forming a deep yellow solution, and the whole distilled in steam. A quantity of a dark red tar was left undissolved, and this was separated, washed with hot water, and dried at 100°. It weighed 11.6 grams and contained only a trace of iron.

The aqueous solutions deposited flocculent, colourless solids on cooling. These were extracted with ether, and gave a total of 6 grams of dry solid, consisting of a mixture of the acids from the compounds formed in the reaction, the extract from the distillate being chiefly *m*-chlorobenzoic acid.

The iron was precipitated from the yellow solution as the hydroxide, and after drying was found to correspond with the total weight of ferric chloride originally present.

#### Summary of Analysis.

Fraction.	Wt. (grams).	Proportion of acids per cent. after hydrolysis.				Original weights of chlorides (grams).				
		Benz. oic.	Monochlorobenzoic.			Benz. zoyl.	Monochlorobenzoyl.			Dichlorobenzoyl.
			m.	o.	p.		m.	o.	p.	
75—80°	42.8	96.6	3.3	0.1		41.4	1.4			
80—98	49.3	25.6	70.6	3.8		12.9	34.5	1.9		
98—99	196.8		90.7	6.3	3.0		178.5	12.4	5.9	
99—100	70.0		88.4	10.3	1.3		61.9	7.2	0.9	
100—103	39.7		72.2	25.7	2.1		28.7	10.2	0.8	
103—105	10.7		60.5	39.5			6.5	4.2		2.2
105—120	29.5		27.6	64.9			8.1	19.2		27.3
120—121	27.3									
Residue	16.9									
483.0						54.3	319.6	55.1	7.6	29.5
Multiplying by $\frac{502}{483}$ to correct for distillation loss (see p. 2517).....										
						56.4	332.2	57.3	7.9	30.7
						397.4				

As the original weight of benzoyl chloride equivalent to the weight (530.2 grams) of reaction mixture taken for distillation = 419.7 grams, the proportions of benzoyl chloride used in producing the final products were as follow (figures given approximated to the nearest 0.5 per cent.):

Unchanged benzoyl chloride.	Monochloro- compounds.	Dichloro- compounds.
13.5%	76%	5.0%

The monochloro-compounds were formed in the proportions

	Meta-.	Ortho-.	Para-.
	83.5%	14.5%	2.0%
or	100	: 17.3	: 2.4

The tarry matter was 2.2 per cent. on the original benzoyl chloride.

*Fractional Crystallisation of the Barium Salts of a Mixture of the Three Monochlorobenzoic Acids.*

A mixture was taken which contained, on analysis by the physical method described, 80.8 per cent. of meta-, 1.5 per cent. of para-, and 17.7 per cent. of ortho-chlorobenzoic acid.

To 40 grams of this mixture in boiling water (750 c.c.) a slight excess (26 grams) of barium carbonate was gradually added. A large amount of barium salt separated and remained undissolved, and the solution was cooled to 50° and filtered. The solid was boiled with a further 600 c.c. of water, which again left some undissolved, the solution cooled to 25° and filtered, and the solid washed with small quantities of water. From this solid the acid (A) was liberated by dissolving it in boiling water, adding a slight excess of dilute hydrochloric acid, cooling, and filtering, and the acid dried at 100°.

The united filtrate containing the rest of the barium salts was fractionally evaporated and kept until the amount of crystals deposited did not increase, and the various fractions of these barium salts were collected, and separately decomposed by dilute hydrochloric acid as above, giving acid mixtures as follows:

	C.c. of liquid.	Acid (grams).	Initial solidifi- cation pt.	M. p. raised by	Composition per cent.
(1)	(A)	22.1	155°	Meta-acid	100 Meta-acid
(2)	800	6.7	153.5	"	98 " "
(3)	460	1.65	152	"	96 " "
(4)	250	0.86	148.5	"	90.5 " "
(5)	170	No crystals deposited.			
(6)	120	0.38	133.5	Para-acid	23 Para-acid
(7)	55	0.4	160.5	"	25.5 " "
(8)	remainder	6.16	138	Ortho-acid	95 Ortho-acid

Fraction (7), recrystallised from light petroleum, finally gave 0.05 gram of the para-acid, m. p. 235—238°.

Thus the above fractional crystallisation proved the presence of *o*- and *p* chlorobenzoic acids. The process also recovered 90 per cent. of the meta-acid present in the original mixture, in a state of 99 per cent. purity, and 81 per cent. of the ortho-acid in a state of 95 per cent. purity.

The assumption that the impurity in the first four fractions was wholly the para-acid, and that the last three fractions were mixtures of the para- and ortho-acids, gives the following analysis :

	Wt. of fraction (grams).	Wt. of acids (grams).		
		Meta-.	Para-.	Ortho-.
(1)	22.1	22.1		
(2)	6.7	6.57	0.13	
(3)	1.65	1.58	0.07	
(4)	0.86	0.78	0.08	
(6)	0.38		0.09	0.29
(7)	0.4		0.1	0.3
(8)	6.16		0.31	5.85
38.25		31.03	0.78	6.44
		= 81.1%	2.0%	16.9%

This result agrees remarkably well with the analysis by the thermal method, as given above [compare the results obtained by Bornwater (*Rec. trav. chim.*, 1912, **31**, 233) when applying a similar method with the calcium salts].

*Method for the Preparation of m-Chlorobenzoic Acid and its Chloride.*

The reaction described affords a ready and comparatively inexpensive method for the preparation of *m*-chlorobenzoic acid in the pure state. Technically, it could be easily carried out as an extension of the method of preparing benzoyl chloride by the direct chlorination of benzaldehyde.

For the laboratory preparation, a quantity of benzoyl chloride is chlorinated in the apparatus described, until the gain in weight is approximately 1.1 times that corresponding with the substitution of one atom of chlorine in the molecule, and the resulting liquid fractionated at a low pressure.

For comparatively pure *m*-chlorobenzoyl chloride (containing some para-compound), continued refractionation with an efficient column is required, the fraction corresponding with 99°/12 mm. being collected.

For the greatest yield of pure *m*-chlorobenzoic acid, the whole fraction corresponding with 96—118°/12 mm. is hydrolysed by boiling with three or four times its weight of water under reflux,

cooled, and the acid filtered off. This is converted into the barium salt, fractionally crystallised from water, and the fractions containing the meta-compound dissolved in boiling water and precipitated with dilute hydrochloric acid. The resulting acid is recrystallised from 30 per cent. acetic acid, and then from benzene to the required purity. A more rapid method, giving a smaller yield, is to collect the fraction corresponding with 97—102°/12 mm., similarly hydrolyse this, and then directly recrystallise the acid from 30 per cent. acetic acid and finally from benzene.

#### *Summary.*

Benzoyl chloride was found to be capable of chlorination in presence of anhydrous ferric chloride.

Analysis of the reaction product was carried out by fractional distillation, hydrolysis of the fractions, and use of a solidification-point method which was worked out for the resulting acid mixtures. The proportions in which the three monochlorobenzoyl chlorides were formed were shown to be : ortho 14.5, meta 83.5, para 2.0 per cent.

The reaction is of value as a method for the preparation of pure *m*-chlorobenzoic acid.

In conclusion, one of us (G. C. R.) desires to express his thanks to the Committee of Scientific and Industrial Research for a grant in 1920—21 which has enabled him to participate in this research.

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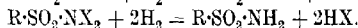
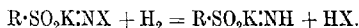
### *CCC.—The Labile Nature of the Halogen Atom in Organic Compounds. Part VI. The Action of Titanous Chloride and of Ammonia on Representative Halogen Compounds.*

By IAN ARMSTRONG BLACK, EDMUND LANGLEY HIRST, and  
ALEXANDER KILLEN MACBETH.

It has already been shown that certain types of organic halogen compounds possess marked oxidising properties, and previous papers in this series have dealt with the removal of the halogen atom from such compounds on treatment with various reducing agents. The reduction of the halogen-substituted nitroparaffins by hydrazine hydrate was examined by Macbeth and Pratt (T., 1921, 119, 1356), and the work was extended to the action of acid reducing agents,

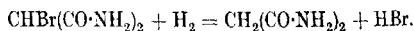
such as titanous chloride, on a similar series of compounds (Henderson and Macbeth, this vol., p. 892). It was shown that under certain conditions of molecular structure the halogen atom was removed, and the nitro-group attacked, during titanium reductions; and attention was directed to the fact that such labile halogen atoms might be regarded as possessing an electropositive character. The action of hydrazine on a further series of substances containing this characteristic type of electropositive halogen was studied by Hirst and Macbeth (this vol., pp. 904, 2169), and it was found that solutions of hydrazine hydrate were readily oxidised by these compounds, nitrogen being quantitatively liberated. The substances found to be reactive include the bromo-derivatives of certain diketones, the chloro- and bromo-derivatives of the malonic esters, and nitrogen-haloids such as the chloroamides, succinchloroimide, and the sulphonchloroamides. It seemed of interest further to extend the work and determine if the halogen atoms in compounds of the above type are susceptible to reduction by titanous salts, and if the oxidising power of the substances is sufficient to liberate nitrogen from ammonia, parallel to the reaction observed with hydrazine hydrate.

The nitrogen-haloids are found to be readily reduced by solutions of titanous chloride, the reaction taking place quantitatively in the cases examined. A quantity of the reagent equivalent to two atoms of hydrogen is required for the reduction of the gram-molecular quantity of the sulphonchloroamides, four equivalents being required for the sulphonchloroamides. The reactions are expressed in the following general equations :



N-Chloroacetanilide, acetobromoamide, succinchloroimide, and succinbromoimide are also quantitatively reduced, a quantity of titanous chloride solution equivalent to two atoms of hydrogen being required for the reduction of the gram-molecular quantity of each of these compounds.

Mono- and di-bromomalonamide are also acted upon by titanous chloride, the bromine atoms being removed in the reduction. Two, and four, equivalents of hydrogen are required for the reduction in the respective cases.



Nitromalonic ester requires six hydrogen equivalents for the reduction of the nitro-group, and ethyl bromonitromalonate requires eight equivalents for the reduction of the gram-molecular quantity.

The bromine atom is therefore removed from the bromonitro-ester during the reaction. This behaviour is in contrast with that of monobromonitromethane on the one hand and that of the bromomalonic esters on the other. The halogen atom in the nitroparaffin withstands the action both of titanous salts and of hydrazine, and the bromomalonic esters, although reactive with hydrazine, are only partly reduced after prolonged treatment with titanous chloride. As the titanium reductions were carried out under similar conditions in all cases, the resistance to reduction can only be ascribed to a difference in the reactivity of the compounds. Marked differences in the reactivities are to be expected from the point of view of the alternate effect in the molecule. The polarities of the oxygen atoms of the nitro-group in bromonitromethane do not endow the halogen atom with an electropositeness sufficient to make it reactive with either hydrazine or titanous salts; in bromonitromalonic ester, the effect of the nitro-group is reinforced by that of the carbethoxy-groups and the very positive bromine atom is readily removed both by hydrazine and by titanous chloride; and in the bromomalonic esters the effect of the carbethoxy-groups makes the halogen sufficiently positive to react with hydrazine, but in the absence of the reinforcing effect of the nitro-group the halogen is not of a sufficiently electropositive nature to be susceptible to reduction by titanous salts.

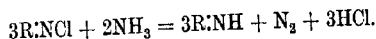
Some observations have already been made on the action of organic halogen compounds on ammonia. Hoffmann (*Ber.*, 1882, **15**, 407) pointed out that aliphatic bromo-amides oxidise ammonia, liberating nitrogen. Willstätter and Hottenroth (*Ber.*, 1904, **37**, 1780) later showed that the bromine atom is removed from ethyl bromonitromalonate when gaseous ammonia is passed into an ethereal solution of the ester, the product being the ammonium salt of ethyl nitromalonate; the same product is obtained when the ester is shaken with strong aqueous ammonia. In contrast with this, it was noted that concentrated aqueous solutions of ammonia acted on methyl bromonitroacetate on long standing, but the halogen atom was not removed, as the product of the reaction was found to be bromonitroacetamide. This behaviour is to be expected, for the halogen in bromonitroacetic ester is not of so positive a character as the bromine in the corresponding malonate, the latter being subjected to the influence of an additional carbethoxy-group.

More recently, Short (*T.*, 1921, **119**, 1445) has shown that the halogen atom is removed from *N*-chloroacetanilide by the action of ammonia, and has based a method of estimation on measurement of the nitrogen evolved when a stream of dry gaseous ammonia is passed into a solution of the halogen compound in dry benzene. In



the present work it is found that ammonia is readily oxidised by many nitrogen haloids, and measurement of the nitrogen evolved shows that the reaction probably takes place quantitatively. The results obtained, however, are slightly low and the reaction cannot be recommended as the basis of a method of estimation, not only on account of the low results obtained, but also by reason of its cumbersome nature compared with the hydrazine method.

Succinchloroimide and succinbromoimide react vigorously with concentrated aqueous solutions of ammonia, the results obtained being from 1—4 per cent. low when calculated according to the equation



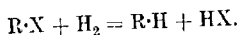
Sulphondichloroamides also react readily with ammonia, but the results obtained in such cases are also about 3 per cent. low.

Aqueous ammonia was found to be without reducing action at the ordinary temperature on the bromomalonic esters, bromomalonamides, the halogen derivatives of diketones such as acetylacetone, 1:1-dimethylcyclohexane-3:5-dione, and cyclohexanespirocyclohexane-3:5-dione. Potassium derivatives of sulphonmonochloroamides, such as chloramine T, were also found to be unattacked.

#### EXPERIMENTAL.

The titanium solutions employed in the reductions were prepared by boiling 500 c.c. of commercial titanous chloride (15 per cent. solution) with 800 c.c. of concentrated hydrochloric acid for a few minutes. The resulting solution was diluted with 3.5 litres of water and transferred to a storage apparatus of the usual type. The solution was standardised with methylene-blue and potassium chlorate.

In the estimations, the substance under examination was boiled gently under reflux for about thirty minutes with an excess of the titanous chloride solution, a slow stream of carbon dioxide being passed through the apparatus during the entire reduction. After cooling, the excess of titanous chloride was determined by direct titration with a standardised solution of iron alum. 19,000 C.c. of the titanous chloride solution were found to be equivalent to 2 grams of hydrogen, so 1 c.c. of the solution corresponds with 0.001866 gram of chlorine or 0.004206 gram of bromine, if the reduction follows the course



The apparatus employed in the estimations with ammonia consists essentially of a narrow-mouthed, graduated cylinder (50 c.c.), a burette, and a 100 c.c. Tennant nitrometer with second limb attach-

ment. The substance under examination is placed in the graduated vessel and covered with a little water. A two-holed stopper is fitted into the mouth of the vessel, the burette being attached through one of the holes whilst a side tube leading to the nitrometer is fitted into the other. The nitrometer is filled with dilute hydrochloric acid. An excess of concentrated aqueous solution of ammonia ( $d$  0.880) is slowly run in from the burette, and the nitrogen evolved drives air over into the nitrometer. The burette is now filled with concentrated hydrochloric acid coloured with litmus, and this is run into the graduated flask until excess of acid is present. The whole apparatus is left for about thirty minutes, and the gas in the nitrometer then measured at atmospheric pressure. The volume of liquid introduced into the graduated vessel is noted and deducted from the volume of the gas measured in the nitrometer.

*N-Chloroacetanilide*.—0.3743 Gram was washed into a small flask and boiled under reflux with 50 c.c. of titanous chloride solution, 39.7 c.c. being required for the reduction. The result corresponds with 19.79 per cent. of chlorine, the percentage purity of the sample being 94.67. Estimation with hydrazine hydrate gave a value of 19.65 per cent. of chlorine, which corresponds with 94.0 per cent. of *N*-chloroacetanilide in the sample.

*Potassium Benzenesulphonchloroamide*.—A sample was dried on the water-bath, and 0.2398 gram, when heated under reflux with titanous chloride solution, required 19.4 c.c. for reduction. The result corresponds with 15.1 per cent. of chlorine (Theoretical, 15.46 per cent.).

*Benzenesulphondibromoamide*.—On heating 0.1500 gram of an impure sample of this substance under reflux with titanous chloride solution, 10.1 c.c. of the reagent were required for the reduction. The result corresponds with 28.31 per cent. of bromine, present as  $\text{NBr}$ , and the percentage purity of the sample is 56.18. Estimations with hydrazine and with potassium iodide gave an average value of 56.5 per cent. for the purity of the compound.

*Acetobromoamide*.—0.2628 Gram required 16.8 c.c. of titanous chloride for reduction. The bromine present as  $\text{NBr}$  therefore amounts to 26.88 per cent., and the sample contains 46.43 per cent. of acetobromoamide. Estimations by the hydrazine method gave a value of 26.84 for the bromine content, corresponding with a percentage purity of 46.3.

*Potassium 2-Nitrotoluene-4-sulphonchloroamide*.—An aqueous solution of this compound was prepared containing 1.4566 grams in 25 c.c., and 2.5 c.c. of this solution, on being heated under reflux with titanous chloride, required 35.89 c.c. for complete reduction. The molecular quantity therefore requires a volume of titanous

chloride solution equivalent to 7.53 (approximately 8) grams of hydrogen. The halogen atom is therefore removed in the reduction.

*Dichloramine T.*—A commercial sample was examined and 0.2396 gram required 34.57 c.c. of titanous chloride for reduction. The sample therefore contains 90.7 per cent. of *p*-toluenesulphondichloroamide. The substance reacts readily with ammonia, nitrogen being liberated almost quantitatively. 0.3580 Gram was found to liberate 21.4 c.c. of nitrogen at 16.5° and 740 mm. This corresponds with a content of 87.7 per cent. of the dichloroamide, the result being about 3 per cent. lower than the values obtained by other methods.

*Succinchloroimide* was quantitatively reduced by titanous chloride, 0.1336 gram requiring 19.05 c.c. of the reagent for complete reduction. This corresponds to a percentage purity of 100.1. The compound reacts with ammonia with the rapid evolution of nitrogen. 0.4020 Gram liberated 24.2 c.c. of nitrogen at 14° and 733 mm., which gives a value for the percentage purity of 98.74. Estimations by the potassium iodide, thiosulphate, and hydrazine methods showed the sample to be pure, and the results obtained with ammonia are therefore low.

*Succinbromoimide.*—A pure sample was examined and gave concordant results in hydrazine, thiosulphate, and titanium estimations. The ammonia value was again low. 0.6920 Gram reacted quickly with ammonia and liberated 30.4 c.c. of nitrogen at 16.5° and 736 mm., which gives a value of 95.63 per cent. for the purity of the sample.

*Ethyl Nitromalonate.*—An alcoholic solution was prepared containing 2.05 grams of nitromalonic ester in 25 c.c., and 2 c.c. of this solution were heated under reflux with titanous chloride solution; 45.1 c.c. of the reagent were required for the reduction. The molecular quantity, therefore, requires a volume of the reagent equivalent to approximately 6 grams of hydrogen, so the reduction of the nitro-group is quantitative.

*Ethyl Bromonitromalonate.*—An alcoholic solution was prepared containing 2.84 grams in 25 c.c., and 2 c.c. required 59.6 c.c. of titanous chloride for complete reduction. The molecular quantity therefore requires a volume of the reagent equivalent to 7.84 grams (approximately 8 grams) of hydrogen. The bromine atom is therefore removed in the reduction.

*Ethyl monobromo-, dibromo-, and isobutylbromo-malonates* were not reduced by titanous chloride solution under ordinary conditions, but on prolonged boiling under reflux of alcoholic solutions of the esters with excess of the reagent reduction took place, upwards of 20 per cent. of the ester being acted upon.

*Ethyl acetyl bromomalonate* was unattacked by titanous chloride even after heating under reflux for two hours.

*Monobromomalonamide*.—0.1884 Gram was dissolved in 20 c.c. of alcohol and gently boiled with 30 c.c. of titanous chloride under reflux for half an hour. 19.0 C.c. of the reagent were oxidised in the reaction, so the molecular quantity of bromomalonamide requires a volume of reagent equivalent to 1.92 grams (approximately 2 grams) of hydrogen for reduction, and therefore the bromine atom is quantitatively removed. The compound is without oxidising action on ammonia.

*Dibromomalonamide*.—0.2683 Gram was dissolved in 20 c.c. of alcohol and heated under reflux with 50 c.c. of titanous chloride solution. 38.36 C.c. of the reagent were oxidised in the reaction, so the molecular quantity of dibromomalonamide requires a volume of the reagent equivalent to 3.92 grams (approximately 4 grams) of hydrogen for reduction. The bromine atoms are therefore removed in the reaction.

*Monobromomalonmethylamide* was not fully reduced by titanous chloride after treatment extending over half an hour. 0.2088 Gram oxidised 16.8 c.c. of the reagent, which corresponds with an 88.5 per cent. reduction.

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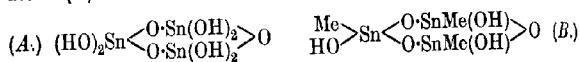
[Received, August 22nd, 1922.]

## CCCL.—*Derivatives of Methylstannonic Acid; Their Bearing upon its Constitution.*

By HERRBERT LAMBOURNE.

It is the object of this paper to show that the so-called methylstannonic acid is not represented by the simple formula  $\text{CH}_3\cdot\text{SnO}\cdot\text{OH}$ , but is probably a complex molecule containing three atoms of tin. Excellent yields of this compound were obtained by modifying Pfeiffer's method of preparation (*Z. anorg. Chem.*, 1910, **68**, 106). This author accepts Hantzsch's view of the quadrivalency of tin in potassium stannite,  $\text{H}\cdot\text{SnO}\cdot\text{OK}$ , and assumes that in the reaction with methyl iodide a methyl group is substituted for the hydrogen atom. The present author would suggest that the name "potassium stannonate" for this quadrivalent tin compound would be preferable to "potassium stannite," in order to distinguish it from the apparently non-existent stannite proper,  $\text{Sn}(\text{OK})_2$ . In view of the undoubted quadrivalence of tin in organic compounds such as

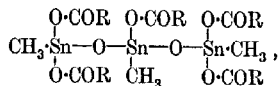
methyl- and ethyl-stannonic acids, the alteration of these names by Glasstone (this vol., p. 65) to, for example, "ethylstannous acid" seems difficult to justify. The term "methylstannonic acid" was originally applied in analogy with the so-called siliconic acids,  $R\cdot SiO\cdot OH$ . These acids, described by Ladenburg (*Annalen*, 1872, **164**, 305; 1874, **173**, 150) and Melzer (*Ber.*, 1908, **41**, 3391), were conclusively proved by Meads and Kipping (*T.*, 1914, **105**, 679; 1915, **107**, 459) to be mixtures of condensed molecules derived from  $R\cdot Si(OH)_3$ . Kipping (*T.*, 1912, **101**, 2108, 2125) has also shown the existence of complex organic silicon compounds such as  $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$  and  $O\begin{smallmatrix} SiPh_2\cdot O \\ \diagup \quad \diagdown \\ SiPh_2\cdot O \end{smallmatrix}$ . Further, the various inorganic silicic acids and silicates are known to be of considerable molecular complexity, silicon showing a marked tendency to form both open and closed chains of silicon and oxygen atoms alternately combined. The probability of the inorganic stannic acids exhibiting a similar tendency would here seem to be indicated. Thus  $\alpha$ -stannic acid,  $H_2SnO_3$ , is usually regarded as being the first anhydro-acid of the ortho-compound,  $Sn(OH)_4$ ; the author would suggest the probability of its being a polymerised substance,  $(H_2SnO_3)_3$ , containing alternately linked tin and oxygen atoms (A).



This cyclic formula would not be out of harmony with the conclusions of Collins and Wood (this vol., p. 443), who indicate a probable mode of condensation of the amphoteric ortho-compound,  $Sn(OH)_4$ , and mention  $(HO)_3Sn\cdot O\cdot Sn(OH)_3$  as a possible first condensation product. It would seem that in the case of the stannic acids, whilst the alkali salts are correctly represented by a comparatively simple structure, the free acids are complex substances. The experimental evidence (*q. v.*) is strongly in favour of methylstannonic acid having the cyclic structure (B).

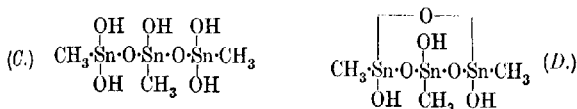
A further point in favour of such a formula is the very slight resemblance of methylstannonic acid to its carbon analogue, acetic acid,  $CH_3\cdot CO\cdot OH$ . The stability of methylstannonic acid, and its insolubility in water and most organic solvents, would indicate a molecular complex, or some condensation product more closely related to the so-called siliconic acids. The nature of the new derivatives about to be described seems to establish fully the constitution of methylstannonic acid, as investigation of their structure showed them all to contain three atoms of tin linked by oxygen atoms. The action of acetic, monochloroacetic, formic, and benzoic

acids, respectively, on methylstannonic acid resulted in the formation of compounds which conformed to the formulæ

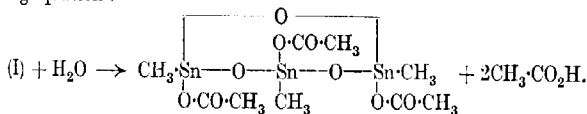


where R = CH<sub>3</sub> (I), CH<sub>2</sub>Cl (II), H (III), and C<sub>6</sub>H<sub>5</sub> (IV), respectively.

The analytical data alone of these compounds were practically sufficient to justify the molecular formulæ, but in addition molecular weight determinations, made with I and II, confirmed the constitutions shown above. At first sight, it would appear that the parent substance, methylstannonic acid, should be similarly represented (C),



being derived from three molecules of the hypothetical ortho-compound, CH<sub>3</sub>Sn(OH)<sub>3</sub>, by loss of water (2 mols.). Such a formula, however, is contrary to the analytical data, which agree with the empirical formula CH<sub>3</sub>SnO·OH. Further condensation, with elimination of another molecule of water, would produce a cyclic compound, the constitution (D) of which receives considerable support from the existence of analogous compounds obtained from the acetyl (I) and formyl (III) compounds. Thus the penta-acetyl derivative on partial hydrolysis produced a much more stable triacetyl compound, which was insoluble in water and all ordinary organic solvents. The reaction may be represented by the following equation :



It will be noted that this triacetyl derivative is a polymerised form of the monoacetyl compound, CH<sub>3</sub>SnO·O·CO·CH<sub>3</sub>. That it conforms to the formula (CH<sub>3</sub>SnO·O·CO·CH<sub>3</sub>)<sub>3</sub>, and not to the simple unimolecular formula, is proved by a molecular weight determination in phenol (cryoscopic). Now the original penta-acetyl compound (I) was formed by the action of excess of glacial acetic acid on methylstannonic acid. If a relatively small amount of acetic acid was brought into contact with methylstannonic acid (about equimolecular proportions), the first product was found

to be identical with that obtained by partial hydrolysis of the penta-acetyl derivative, namely, the triacetyl compound. Further, prolonged contact of this latter substance with boiling glacial acetic acid was required before reconversion into the penta-acetyl compound occurred. These facts would seem to indicate that the triacetyl derivative is very similar in constitution to methylstannonic acid, and were taken as evidence of the termolecular structure of the latter. Continued action of acetic acid on the triacetyl compound broke open the ring and produced the penta-acetyl compound. It might be expected that complete rupture of the ring would occur with formation of three molecules of the triacetyl derivative,  $\text{CH}_3\text{Sn}(\text{O}\cdot\text{CO}\cdot\text{CH}_3)_3$ , of the trihydroxide,  $\text{CH}_3\text{Sn}(\text{OH})_3$ . It is possible that this actually does take place in the acetic acid solution, but the ortho-acetyl compound is too unstable to be isolated; on keeping the solution after concentration, condensation occurs and the more complex penta-acetyl derivative separates. Finally, a quantitative conversion of the penta-acetyl derivative into the triacetyl compound was effected and the result was in close agreement with that demanded by the equation given above.

A compound corresponding with this triacetyl derivative was obtained in a similar manner by partly hydrolysing the penta-formyl compound. This triformyl compound (constitution analogous to *D*) resembled the triacetyl derivative, being apparently of the same crystalline (rhomboidal) form, and showed similar stability towards water and ordinary organic solvents.

A pentabenzoyl derivative was produced by the reaction between methylstannonic and benzoic acids, and analysis showed it to be of the same constitution as the other penta-substituted derivatives.

Further work is proceeding to prove as completely as possible the constitution of this new type of derivative from methylstannonic acid. Attempts are also being made to produce analogous compounds of ethylstannonic acid.

## EXPERIMENTAL.

### *Methylstannonic Acid.*

Pfeiffer's method (*loc. cit.*) was modified as follows: To a solution of freshly prepared stannous chloride (42 grams) in water (100 c.c.) at  $0^\circ$  was slowly added, with stirring, potassium hydroxide (100 grams) in water (400 c.c.). When nearly all the alkali had been run in, the precipitate first formed almost entirely redissolved, and the residue turned black, which was taken as an indication of the completion of the reaction. To the filtered solution methyl iodide

(30 grams) and sufficient ethyl alcohol (about 250 c.c.) were added to make the solution homogeneous. Three days afterwards, carbon dioxide was passed through the solution (under pressure), saturation being indicated by only faint alkalinity towards litmus. The heavy, white, crystalline precipitate of potassium methylstannoyl carbonate,  $\text{CH}_3\text{SnO}\cdot\text{O}\cdot\text{CO}_2\text{K}$  (Pfeiffer, *loc. cit.*) was filtered off, decomposed by boiling with water, and the precipitated methylstannonic acid was washed thoroughly with boiling water. The yield was 29 grams and a further 8 grams was obtained by evaporation (on a water-bath) of the filtrate from the potassium methylstannoyl carbonate.

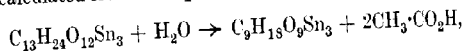
*Penta-acetyl Compound* (Formula I).—Methylstannonic acid dissolved readily in excess of boiling glacial acetic acid to give a slightly turbid, brown solution, which was filtered and concentrated. On prolonged keeping, crystalline nodules separated, which dissolved in hot acetic acid much more readily than did methylstannonic acid. Crystallisation also occurred more easily, although the solution exhibited a high degree of supersaturation. Repeated crystallisation from acetic acid gave a product, flat prisms, which was washed with dry ether and dried over sodium hydroxide in a vacuum desiccator. This *penta-acetyl* derivative, which appeared perfectly homogeneous under the microscope, did not melt, but began to decompose at about  $250^\circ$ , and on complete ignition left a residue of stannic oxide. Atmospheric moisture hydrolysed the compound with liberation of acetic acid; small quantities of water and ethyl alcohol produced a partly hydrolysed triacetyl derivative in rhomboidal crystals. It would appear that solution was effected in the first instance, followed by immediate precipitation of the more stable triacetyl compound; similar results, produced by ordinary chloroform and carbon tetrachloride, were probably due to small amounts of water present in these solvents. Excess of water brought about complete hydrolysis to methylstannonic and acetic acids.

Tin was estimated after cautious ignition with a few drops of fuming nitric acid and concentrated sulphuric acid, the final product being stannic oxide. Estimation of acetyl groups was carried out by Perkin's method and also by the benzenesulphonic acid method. The molecular weight determination was carried out in boiling glacial acetic acid (Found: C=21.34, 21.50; H=3.31, 3.40; Sn=48.96, 49.01;  $\text{CH}_3\cdot\text{CO}$ =29.62, 29.78;  $M$ =713.  $\text{C}_{13}\text{H}_{21}\text{O}_{12}\text{Sn}_3$  requires C=21.40; H=3.29; Sn=48.98;  $\text{CH}_3\cdot\text{CO}$ =29.49 per cent.;  $M$ =729).

*Triacetyl Compound*.—The action of a small quantity of glacial acetic acid on methylstannonic acid (slightly less than equal mole-



cular proportions) first changed the latter from a white, amorphous powder to a granular, crystalline substance, which was also obtained by partial hydrolysis of the penta-acetyl derivative with a small amount of water or alcohol. This derivative was best obtained, however, by adding excess of alcohol to the acetic acid solution of the penta-acetyl compound; on warming on a water-bath, or on long keeping at the ordinary temperature, the triacetyl compound was produced in quantitative yield. All these methods gave the compound in rhomboidal crystals, which were washed with hot alcohol and dried at  $100^{\circ}$ , or in a vacuum desiccator. Microscopical examination showed that the compound was homogeneous, and this had to be taken as the only criterion of purity, owing to its insolubility in nearly all organic solvents. Heating decomposed it (without melting) at about  $280^{\circ}$ , leaving a residue of stannic oxide. This triacetyl compound was very stable; very prolonged boiling with glacial acetic acid reconverted it into the penta-acetyl derivative; similar treatment with water eventually brought about complete hydrolysis into acetic and methylstannonic acids. The compound dissolved in phenol apparently unchanged, because alcohol or ether reprecipitated the substance in its original form (Found: C = 17.16, 16.98; H = 2.75, 2.78; Sn = 56.90, 56.99;  $\text{CH}_3\cdot\text{CO}$  = 20.34, 20.20;  $M$ , in freezing phenol, = 621.  $\text{C}_9\text{H}_{18}\text{O}_9\text{Sn}_3$  requires C = 17.23; H = 2.87; Sn = 56.94;  $\text{CH}_3\cdot\text{CO}$  = 20.58 per cent.;  $M$  = 627). A weighed amount of the penta-acetyl derivative, repeatedly evaporated to dryness with a small quantity of alcohol, yielded 85.13 per cent. of the triacetyl compound. The theoretical yield, calculated from the equation



is 86.02 per cent.

*Monochloroacetyl Compound (II).*—Boiling monochloroacetic acid (10 grams) was saturated with methylstannonic acid, and the cooled semi-liquid mass extracted with hot benzene. The minute rhombohedra deposited in the cooled extract were repeatedly crystallised from boiling benzene, the monochloroacetyl compound obtained melting at  $214\text{--}224^{\circ}$  with decomposition. It was soluble in alcohol or acetone and apparently hydrolysed by water. A partly hydrolysed derivative corresponding to the triacetyl compound has not been obtained (Found: Sn = 39.59, 39.50; Cl = 19.65, 19.61;  $M$ , in boiling benzene, = 899, 916.  $\text{C}_{13}\text{H}_{19}\text{O}_{12}\text{Cl}_2\text{Sn}_3$  requires Sn = 39.61; Cl = 19.69 per cent.;  $M$  = 901.5).

*Pentaformyl Compound (III).*—To anhydrous formic acid heated to boiling, small quantities of methylstannonic acid were added until the solution became rather viscous. With some difficulty, very

fine, needle-shaped crystals were obtained by concentrating the solution in a vacuum at the ordinary temperature, and recrystallisation from formic acid was performed in the same way. Decomposition (without melting) began at about  $240^{\circ}$  and appeared to be complete at about  $280^{\circ}$ , the usual residue of stannic oxide being obtained. This pentaformyl compound was readily soluble in water, complete hydrolysis to methylstannonic and formic acids occurring on boiling. Treatment with alcohol produced a triformyl derivative (Found: C = 14.46, 14.42; H = 2.27, 2.15; Sn = 54.26, 54.30.  $C_8H_{14}O_{12}Sn_3$  requires C = 14.56; H = 2.24; Sn = 54.18 per cent.).

*Triformyl Compound.*—The triformyl derivative of methylstannonic acid corresponding with the triacetyl compound was prepared in a similar manner, namely, partial hydrolysis with ethyl alcohol. Excess of alcohol was added to a formic acid solution of the pentaformyl compound; on warming for a short time on the water-bath, the triformyl compound separated in rhomboidal crystals. Prolonged heating was inadvisable, as further hydrolysis or decomposition apparently occurred with separation of a flocculent precipitate. The compound was filtered, washed with warm alcohol, and dried in a vacuum desiccator. Evidence of purity was again dependent on microscopical examination, as the compound could not be recrystallised owing to its insolubility in water and most organic solvents. In this respect it resembled its stable triacetyl analogue. It decomposed, without melting, at about  $270^{\circ}$  (Found: C = 11.97, 11.95; H = 1.96, 2.05; Sn = 60.88, 60.85.  $C_6H_{12}O_9Sn_3$  requires C = 12.31; H = 2.05; Sn = 61.02 per cent.).

*Pentabenzoyl Compound (IV).*—Preliminary experiments were made with the penta-acetyl compound, which was found to dissolve in fused benzoic acid with expulsion of acetic acid. The anticipation that a corresponding pentabenzoyl derivative would be produced was realised, as the residue left after extraction with ether was found to have the expected composition. A purer compound was obtained as follows: To fused benzoic acid (12 grams), methylstannonic acid was added in small quantities so long as a clear solution was formed, 4 grams being the maximum amount which could be added. If the temperature was allowed to rise above  $200^{\circ}$ , the mass darkened considerably and an impure, yellow product resulted. While still molten, the mass was poured on a cold tile, then finely ground and repeatedly extracted with ether in order to remove unchanged benzoic acid. The white residue (7 grams) melted at  $280$ – $285^{\circ}$ , and was completely soluble in boiling acetone, from which it crystallised in minute rhombohedra melting at about  $272^{\circ}$ . It was apparently insoluble in water, but readily

soluble in ethyl alcohol and sparingly soluble in ethyl acetate  
(Found: C = 43.56, 43.65; H = 3.50, 3.55; Sn = 34.49, 34.54.  
 $C_{38}H_{34}O_{12}Sn_3$  requires C = 43.88; H = 3.28; Sn = 34.38 per cent.).

The author thanks Professor F. S. Kipping, F.R.S., for suggesting this research, and for his valuable criticism and advice.

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[Received, August 18th, 1922.]

## CCCII.—A Simplified Method for the Resolution of *Methyl-n-hexylcarbinol*.

By JOSEPH KENYON.

SOME years ago a method of resolving *sec*.-octyl alcohol (methyl-*n*-hexylcarbinol) into its optically active forms was described by Pickard and Kenyon (T., 1907, **91**, 2058) which may be briefly described as follows: The alcohol is converted into its hydrogen phthalic ester by heating with phthalic anhydride and this in turn is converted into its brucine salt, which is fractionally crystallised from acetone until constant rotation is reached. By this means, the optically pure, dextrorotatory form of the hydrogen phthalic ester is obtained and this on hydrolysis yields the optically pure dextro-alcohol. The more soluble portions of the brucine salt are decomposed, when a hydrogen phthalic ester of fairly high *laevo* rotation is obtained; this is combined with cinchonidine, and the cinchonidine salt crystallised from acetone until optical purity is reached. In this way, the optically pure *laevo*-alcohol is obtained.

This method of resolving *sec*.-octyl alcohol works quite smoothly and gives good results, but it suffers from two drawbacks which become considerable when relatively large amounts of material are employed; in the first place, the solubility in acetone of the brucine salt of *d-sec*.-octyl hydrogen phthalate is very much less than that of the corresponding *dl*- or *l*-compound, and although this has the great advantage of giving a very sharp separation of the *d*- and the *l*-isomerides, yet it has the inevitable drawback from the practical point of view of requiring the employment of large volumes of acetone, this having proved itself by far the most useful of the commoner solvents for this purpose. The second drawback arises from a cause of an opposite character; the solubility of the cinchonidine salt of *l-sec*.-octyl hydrogen phthalate is not considerably less than that of the *dl*-form, and consequently the separation

of the optically pure *l*-form of the hydrogen phthalate requires a larger number of crystallisations of the cinchonidine salt, and the proportion obtained is also much less than is the case with the brucine salt.

As fairly large quantities of the optically pure forms of *sec*.-octyl alcohol were required in the course of some work, experiments were initiated with the view of increasing the convenience and, if possible, the efficiency of the method outlined above, and the following results have been obtained.

It has been found that the optically active modifications of *sec*.-octyl hydrogen phthalate are much less soluble in acetic acid than the inactive modification, and that, in consequence, the crystallisation of a partly resolved sample rapidly gives the optically pure form of *sec*.-octyl hydrogen phthalate.

The procedure can perhaps be most concisely described by giving the details of an actual experiment, and this is done in the experimental portion of this paper. It will be seen that the employment of large volumes of acetone is avoided and the use of cinchonidine dispensed with altogether. In addition, the actual labour involved is probably only about one-tenth of that required by the original method, and the saving of time correspondingly great.

As the conversion of *sec*.-octyl alcohol into its hydrogen phthalic ester and its regeneration from this by hydrolysis are both almost quantitative reactions, it will be seen that the optically active *sec*.-octyl alcohols become substances which are readily available in considerable amounts.

#### EXPERIMENTAL.

To a warm solution of *sec*.-octyl hydrogen phthalate (278 grams) in acetone (600 c.c.) is added brucine (394 grams), and the mixture warmed until solution is complete. After cooling, the crystals of brucine salt (A) are filtered off, pressed, and washed in the funnel with acetone (250 c.c.) to remove adhering mother-liquor. The combined filtrate and washings are concentrated to about half bulk and poured into dilute hydrochloric acid, when the hydrogen phthalic ester separates as an oil which quickly sets to a crystalline mass. It is filtered off, washed with cold water, and spread on porous plate. It is not necessary to dry the product, but if this is done, it is found that its weight is approximately one-half of that of the hydrogen phthalate originally taken, and that it has the rotation in 5 per cent. solution in absolute alcohol of  $[\alpha]_{5461} = 47^\circ$ .

The crystals A are dissolved in the minimum amount of hot ethyl alcohol and decomposed by pouring the solution into dilute hydrochloric acid. The weight of hydrogen phthalic ester obtained

is about half of that originally taken and its rotation is about  $[\alpha]_{5461} + 47^\circ$ .

These two lots of partly active *sec.*-octyl hydrogen phthalate are now separately crystallised twice from acetic acid (about twice their weight of 90 per cent. acetic acid being required for solution in each case), when they are obtained in an optically pure condition and possess the rotations  $[\alpha]_{5461} - 58.5^\circ$  and  $[\alpha]_{5461} + 58.3^\circ$ , respectively.

The amount of pure product obtained in each case was, respectively, 99 grams and 96 grams, corresponding to a yield of 70 per cent. of that theoretically possible.

BATTERSEA POLYTECHNIC.

[Received, October 17th, 1922.]

### CCCLIII.—Decomposition of Dithiocarbazinates.

By SIMA M. LOSANTCH.

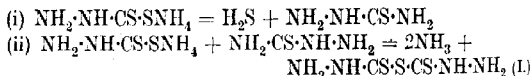
IN the decomposition accompanying the evaporation on the water-bath of an aqueous or alcoholic solution of ammonium or substituted ammonium dithiocarbazinate (T., 1921, 119, 764), two stages are recognisable; at first, hydrogen sulphide only is evolved, and towards the end ammonia. The formation of the ammonium sulphide is evidently due to initiation of the second reaction before the first is completed.

The first reaction, in the case of hydrazine dithiocarbazinate,

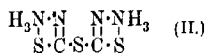


gives rise to thiocarbohydrazide, which is obtained pure by crystallisation of the dry residue from boiling water (m. p.  $169^\circ$ . Found: N = 52.7 per cent.); the mother-liquor contains the easily soluble, acid product resulting from the second stage of the decomposition, to which reference is made below.

Ammonium dithiocarbazinate behaves differently under comparable conditions, for the expected thiosemicarbazide immediately undergoes further changes, culminating in the formation of the acid product (II) finally isolated; it probably reacts with unchanged ammonium dithiocarbazinate to yield, in the second stage of the decomposition, ammonia and dithiocarbazinic thio-anhydride (I),

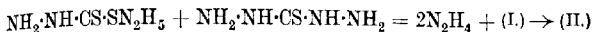


which isomerises to the modification  $\begin{array}{cc} \text{NH}_2\cdot\text{N} & \text{N}\cdot\text{NH}_2 \\ | & | \\ \text{HS}\cdot\text{C}\cdot\text{S}\cdot\text{C}\cdot\text{SH} \end{array}$  or



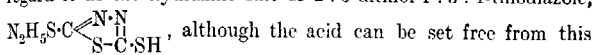
Behaviour analogous to the preceding is shown by alkylammonium dithiocarbazinates when treated in a similar manner. As a result of a side reaction in all these cases, a small amount of thiocarbohydrazide is formed.

The same acid product (II) is also obtained by prolonged heating of hydrazine dithiocarbazinate in solution :



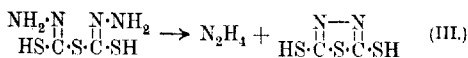
It is to be noted, in support of the preceding explanation of the mechanism of the decomposition, that thiocarbohydrazide alone, under comparable conditions, remains unaltered, and that the thio-anhydride (I or II) is obtained only when the primary dithiocarbazinate is also present.

The thio-anhydride (I or II), the ultimate product of decomposition of all dithiocarbazinates, has already been prepared in one operation by Busch (*Ber.*, 1894, **27**, 2518) by heating an alcoholic solution of carbon disulphide, hydrazine sulphate, and potassium hydroxide for three hours on the water-bath. He is inclined to regard it as the hydrazine salt of 2 : 5-dithiol-1 : 3 : 4-thiodiazole,



although the acid can be set free from this hydrazine salt not by dilute, but only by concentrated hydrochloric acid, an indication that the strong acid produces a profound change in the structure of the substance.

In view of the facts mentioned above, it is obvious that the dithiocarbazinate is the parent substance of the thio-anhydride, and therefore the proposed constitution (I or II) is more probable than that of Busch, the more so as it is scarcely conceivable that a hydrazine salt could have been produced under the experimental condition he employed, namely, an excess of alkali. The formation of the dithiolthiodiazole by the action of concentrated hydrochloric acid would therefore be represented as follows :



#### EXPERIMENTAL.

*Dithiocarbazinic thio-anhydride* (Formula I or II) is obtained together with sulphur when an aqueous or alcoholic solution of any of the above-mentioned dithiocarbazinates is evaporated to dryness. The residue is dissolved in boiling water, the solution filtered from sulphur, cooled to remove thiocarbohydrazide by crystallisation, and the filtrate again evaporated to dryness. The residue crystallises from alcohol in needles or small plates, which

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change at about 170° and melt at 225°. The thio-anhydride is readily soluble in water, but less soluble in alcohol (Found : C = 13.24; H = 3.59; N = 31.20; S = 53.20.  $C_2H_6N_4S_3$  requires C = 13.19; H = 3.30; N = 30.77; S = 52.74 per cent.).

With methyl iodide the thio-anhydride yields 2 : 5-dimethylthiol-1 : 3 : 4-thiodiazole, identical with the ether derived from the dithiol-thiodiazole (below).

2 : 5-Dithiol-1 : 3 : 4-thiodiazole (Formula III) (compare Busch, *loc. cit.*) is most conveniently prepared by adding, with cooling, 17 grams of carbon disulphide to a solution of 10 grams of hydrazine hydrate in 100 c.c. of alcoholic ammonia. The mixture is evaporated on the water-bath, the residue dissolved in boiling water, the solution filtered from sulphur and mixed with an equal volume of alcohol, and concentrated hydrochloric acid added until crystals begin to separate, which will fill the solution when it shall be cooled (yield 18 grams). If the addition of alcohol is omitted, the substance will be precipitated in very small crystals. Litmus paper is reddened and subsequently bleached by the aqueous solution of the thiodiazole.

The ammonium salt is converted by methyl iodide to the dimethyl ether obtained by Ziegele (*J. pr. Chem.*, 1899, [ii], 60, 42), white crystals, m. p. 136—137° (Found : C = 26.41; H = 3.02; N = 15.82. Calc., C = 26.96; H = 3.37; N = 15.73 per cent.).

2-Thiol-1 : 3 : 4-thiodiazolyl Sulphides.

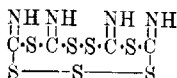
The monosulphide,  $\begin{array}{c} \text{N} \cdots \text{N} \quad \text{N} \cdots \text{N} \\ | \quad | \quad | \quad | \\ \text{HS} \cdot \text{C} \cdot \text{S} \cdot \text{C} \cdot \text{S} \cdot \text{C} \cdot \text{S} \cdot \text{C} \cdot \text{SH} \end{array}$ , is obtained when an aqueous or alcoholic solution of 2 : 5-dithiol-1 : 3 : 4-thiodiazole is boiled, or heated on the water-bath, for several days with renewal of the evaporated water; during the progress of the reaction, hydrogen sulphide is liberated :  $2C_2H_2N_2S_3 = H_2S + C_4H_2N_4S_5$ .

The monosulphide crystallises in faintly yellow needles, which melt and decompose at 173°, and is readily soluble in alcohol or ether, and sparingly soluble in water (Found : C = 18.65; H = 1.09; N = 20.70.  $C_4H_2N_4S_5$  requires C = 18.05; H = 0.75; N = 21.05 per cent.).

This monosulphide forms with alkali and ammonia salts which are readily soluble in water; those of the heavy metals are insoluble. The silver and lead salts are yellow, the copper salt brown, and the cobalt salt green.

The dimethyl ether,  $S(C_2N_2S \cdot SMe)_2$ , obtained from the ammonium salt and methyl iodide, forms colourless crystals, m. p. 71°, and is soluble in alcohol (Found : N = 19.71.  $C_6H_6N_4S_5$  requires N = 19.05 per cent.).

The Disulphide,  $S_2(C_2HN_2S_2)_2$ , and Polysulphide,  $C_4H_4N_4S_7$ .—The disulphide was prepared by Ziegler by the action of iodine on an alcoholic solution of 2:5-dithiol-1:3:4-thiodiazole. I find, however, that if the alcoholic solution is boiled with an excess of iodine, in addition to this disulphide there is formed a crystalline, yellow polysulphide, m. p.  $186^\circ$ , which is insoluble in alcohol. It is not identical with the polysulphide,  $(C_2H_2N_2S_3)_n$ , obtained by Ziegler from the dithiolthiodiazole by means of ferric chloride, and has probably the structure



(Found: C = 15.19; H = 1.10; N = 17.24; S = 67.50.  $C_4H_4N_4S_7$  requires C = 14.46; H = 1.20; N = 16.87; S = 67.47 per cent.).

I desire to express my thanks to Mr. D. Yovanovitch for some assistance in the analytical portion of the work.

CHEMICAL INSTITUTE OF THE  
UNIVERSITY, BELGRADE.

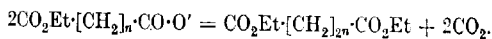
[Received, August 1st, 1922.]

#### CCCIV.—*Electro-synthesis of Azelaic and Thapsic Acids.*

By MABEL CARMICHAEL.

At the suggestion of Professor Sir James Walker I undertook the electrosynthetic preparation of *n*-heptanedicarboxylic acid and of *n*-tetradecanedicarboxylic acid in order to compare them with azelaic acid and thapsic acid derived from natural sources.

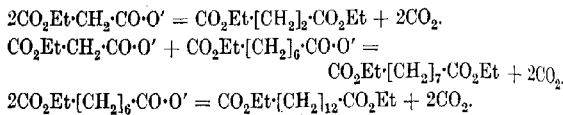
The electrosynthesis of dibasic acids as carried out by Crum Brown and Walker led in every case to the ester of an acid with an even number of carbon atoms, thus:



In order to prepare the ester of an acid with an odd number of carbon atoms, such as  $\text{CO}_2\text{Et} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{Et}$ , it is necessary to electrolyse, not a single ester-salt, but a mixture of ester-salts, one with an odd and the other with an even number of carbon atoms, so that by addition the resulting number will be odd. Thus *n*-heptanedicarboxylic acid, which contains 7  $\text{CH}_2$  groups, might be prepared from pairs of acids containing respectively 2 and 5, 4 and 3, or 6 and 1  $\text{CH}_2$  groups. The selection of the particular pair will in general be determined by the ease of preparation of the original ester-salts and by the ease of separation of the resulting



esters or the acids obtained from them. In the present instance, the most suitable combination is that of suberic acid,  $\text{CO}_2\text{H}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$ , with malonic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , the original substances being readily obtainable and the resulting dibasic acids easily separable. The main organic products of the electrolysis of the mixture of the sodium ethyl compounds of these acids would be ethyl succinate, ethyl *n*-heptanedicarboxylate, and ethyl *n*-dodecanedicarboxylate produced according to the equations :



By using excess of the malonic acid compound, we may increase the proportion of the *n*-heptano acid relatively to the *n*-dodecano acid, the large quantity of succinic acid formed simultaneously being easily removable owing to its solubility in water. *n*-Heptanedicarboxylic acid was synthesised in this way and proved to be identical with azelaic acid from the oxidation of castor oil, an identity which had already been established by a purely chemical method by Haworth and Perkin (T., 1894, 65, 86).

By electrolysis the sodium ethyl compound of azelaic acid, ethyl *n*-tetradecanedicarboxylate was obtained. The acid resulting from the hydrolysis of this ester was proved to be identical with thapsic acid derived from *Thapsia*. During the progress of this work, Stosius and Wiesler (*Biochem. Z.*, 1920, 108, 75) published a paper on the same subject. Their identification was based, however, on qualitative solubilities and a melting-point determination, and further confirmation was thought desirable.

#### EXPERIMENTAL.

*Preparation of Suberic and Azelaic Acids from Castor Oil.*—The method followed was a modification of that of Markownikoff (*Ber.*, 1893, 26, 3089; compare Day, Kon, and Stevenson, T., 1920, 117, 641). Instead of nitric acid being added to castor oil, the oil (200 grams) was run in successive small quantities into nitric acid (400 grams of *d* 1.25) contained in a flask fitted with an efficient mechanical stirrer. To start the reaction 1 gram of sodium nitrite was added to the nitric acid. The oxidation proceeded quietly and was completed by heating the flask for half an hour on a sand-bath after all the castor oil had been added. The resulting product was repeatedly extracted with boiling water, the aqueous solutions on evaporation to small bulk and crystallisation yielding 40 grams

of solid mixed acids. A somewhat better yield was obtained by first hydrolysing the castor oil and oxidising the acids obtained from it. Titration of the mixed acids obtained by oxidation showed that they were present in the approximate proportion of 1 part of azelaic acid to 2 parts of suberic acid.

The method employed by Markownikoff for the separation of the two acids proved to be both tedious and unsatisfactory, and the following scheme was substituted. Advantage was taken of the greater solubility of azelaic acid in ether (2.7 parts per 100, as against 0.8 part of suberic acid). Calculating from these solubilities and the composition of the mixed acids, a quantity of ether was taken just sufficient to dissolve the azelaic acid. Solution was effected in a closed bottle provided with a mechanical stirrer. After one and a half hours, the contents were filtered through a Buchner funnel. The filtrate contained all the azelaic acid and a small proportion of suberic acid. After evaporation of the ether, the composition of the residual mixture was ascertained by titration of a weighed portion. Water was then added in the quantity just necessary to keep the more soluble suberic acid in solution at 15°. The temperature was then raised until the acids had completely dissolved. On cooling, glistening, flaky crystals of azelaic acid separated, the melting point being 102–104°. Recrystallisation from benzene gave the pure acid melting at 106°.

The crude suberic acid (m. p. 130–135°) left in the Buchner funnel was purified by boiling with a small quantity of benzene, in which azelaic acid is easily soluble and suberic acid very sparingly soluble. The purified product melted at 139°. With this method of separation, 200 grams of the crude mixed acids yielded 106 grams of pure suberic acid and 64 grams of pure azelaic acid.

#### *Electrosynthesis of Azelaic Acid.*

Suberic acid obtained in the manner described above was converted first into ethyl suberate and then into potassium ethyl suberate by the customary methods. A 50 per cent. aqueous solution of the ester-salt was prepared and mixed with a 50 per cent. aqueous solution of potassium ethyl malonate, in such proportion as to give 1 mol. of suberate to 3 mols. of malonate. The mixed solution was electrolysed in a platinum crucible, which acted as cathode, the anode being formed of a spiral of stout platinum wire. The current averaged 1.7 amperes with a voltage of 7.5, and the temperature was kept at 15° by external water-cooling. After two hours' electrolysis, 4 c.c. of a pale yellow oil were obtained from 20 c.c. of solution. In all, 2.3 grams of this oil were obtained.

The oil was subjected for a short time to steam distillation in order to remove low-boiling esters of monobasic acids. The residual oil was saponified with potassium hydroxide. The acids liberated from the solution of potassium salts formed a sludgy precipitate, from which were ultimately separated succinic, azelaic, and *n*-dodecanedicarboxylic acids in accordance with the theoretical prediction. The separation was effected by means of water at 60°, with filtration at the same temperature. Under these conditions, *n*-dodecanedicarboxylic acid is very sparingly soluble and may be separated by filtration. From the filtrate *n*-heptanedicarboxylic acid crystallises on cooling, whilst succinic acid remains in solution. The *n*-heptanedicarboxylic acid obtained in this way melted at 103°, and on recrystallisation from benzene at 106° [Found: C = 57.46; H = 8.49. Calc. for  $C_9H_{18}O_6$ , C = 57.45; H = 8.51 per cent. Replaceable hydrogen by titration, 1.06; calc. for  $C_7H_{14}(CO_2H)_2$ , 1.06]. The acid in appearance and crystalline habit was similar to azelaic acid prepared from castor oil, and their complete identity was established by the mixture of the two acids melting sharply at 106°.

*Electrosynthesis of Thapsic Acid.*

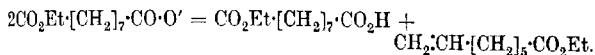
Azelaic acid, prepared from castor oil, was converted into ethyl azelate, which was mixed with 25 parts of rectified spirit and half saponified in stages with potassium hydroxide in the cold. The potassium ethyl salt obtained after evaporation was freed from dipotassium salt by extraction with absolute alcohol, in which the latter is insoluble. A 50 per cent. aqueous solution of the potassium ethyl salt was electrolysed under the same conditions as previously described, the current averaging 2 amperes. The oily layer produced (23 grams from 62 grams of azelaic acid) was removed by means of ether. The residue after evaporation of the ether was subjected to steam distillation until no more oil was carried over. A greasy solid remained on cooling, which was spread on porous tile and subsequently recrystallised from methyl alcohol. Finally, a pure white, finely crystalline solid (17 grams) was obtained (Found: C = 70.33, 70.15; H = 11.02, 11.11. Calc. for  $C_{20}H_{38}O_6$ , C = 70.19; H = 11.11 per cent.). The product had thus the composition of the ethyl ester of tetradecanedicarboxylic acid and from its mode of formation must possess normal constitution. It melted sharply at 39°.

A portion of the ester was saponified with sodium hydroxide in boiling methyl alcohol solution. The alcohol was distilled off after completion of the action, and the aqueous solution of the residual sodium salt was acidified with hydrochloric acid. A

gelatinous precipitate was obtained which was extracted with ether and recrystallised from that solvent [Found: C = 67.02; H = 10.47. Calc. for  $C_{16}H_{20}O_4$ , C = 67.13; H = 10.49 per cent. Replaceable hydrogen by titration: found 0.70; calc. for  $C_{14}H_{28}(CO_2H)_2$ , 0.71].

The melting point,  $124^\circ$ , and the solubility of the acid in various solvents pointed to its identity with the acid of the same composition obtained by Canzoneri (*Gazzetta*, 1883, **13**, 514) from the resin of *Thapsia garganica* and named by him thapsic acid. The identity was further established by preparation of the anhydride and the anilide. The anhydride was prepared by boiling with acetic anhydride. On recrystallisation from ligroin, it was found to melt at  $71^\circ$ , the same melting point as that given by Canzoneri. The anilide was prepared by heating the acid in a sealed tube with excess of aniline for eight hours at  $180^\circ$ . The contents of the tube, on cooling, were shaken with dilute hydrochloric acid and ether. The ethereal layer was dried and distilled; the anilide remained as a pale violet solid, which, on recrystallisation from alcohol, melted at  $163^\circ$ . Canzoneri gives the melting point  $162-163^\circ$ .

*Ethyl n-Heptenecarboxylate*.—According to the scheme put forward by Crum Brown and Walker for the electrolysis of the ester-salts of dibasic acids, a subsidiary product of the electrolysis of ethyl potassium azelate would be ethyl *n*-heptenecarboxylate, formed according to the equation



This ester should be found in the portion of the electrolysed product volatile with steam. The steam distillate was accordingly extracted with ether, and the ethereal solution after drying was subjected to distillation. After removal of the ether the small quantity of oil remaining distilled for the most part at  $210-212^\circ$ . It decolorised bromine, and also alkaline potassium permanganate in the cold (Found: C = 70.44, 70.61; H = 10.71, 10.51. Calc. for  $C_{16}H_{18}O_2$ , C = 70.58; H = 10.58 per cent.). The ester had thus the expected composition and properties. The boiling point, as found by the method of Smith and Menzies, was  $210^\circ$ .

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CCCV.—*The Action of Bromine Water on Indene.*

By JOHN READ and ERIC HURST.

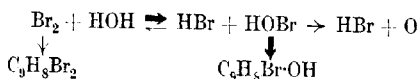
IN a series of communications dealing with the action of chlorine water and bromine water on unsaturated substances, it has been shown that these reagents function with unsuspected ease as sources of potential hypochlorous and hypobromous acids. In the case of ethylene (T., 1917, **111**, 240; 1920, **117**, 359, 1214), owing to the gaseous nature and slight solubility of the hydrocarbon, the reaction is comparatively slow, and, in accordance with the generally accepted view, the formation of halogenohydrin is promoted by cooling. The similar but much more rapid reactions which lead to the formation of halogenohydrins from cinnamic acid and certain substituted cinnamic acids (T., 1921, **119**, 1774) and from allyl alcohol (this vol., p. 989) likewise yield the most satisfactory results at low temperatures. These observations might therefore be correlated with the tendency of hypochlorous and hypobromous acids to undergo decomposition when heated in dilute aqueous solution. Such decomposition, however, appears also to be accelerated by sunlight, whereas in no instance in this series of investigations has sunlight proved detrimental to halogenohydrin formation; the formation of ethylenebromohydrin, indeed, appears to be promoted by conducting the reaction in bright sunlight (*loc. cit.*, p. 1221).

It was thus of particular interest to discern, in the interaction between bromine water and indene, an instance of halogenohydrin formation which appeared to be promoted by the application of heat. The bromohydrin in question, 2-bromo-1-hydroxyhydrindene, was originally prepared in very unsatisfactory yield by the prolonged action of boiling aqueous alcohol on dibromohydrindene (Krämer and Spilker, *Ber.*, 1890, **23**, 3276). Later, in utilising this substance for the preparation of 1-hydroxy-2-hydrindamine, Pope and Read (T., 1912, **101**, 760) showed that it could be obtained rapidly, in 85 per cent. yield, by adding bromine, dissolved in potassium bromide solution, to an emulsion of indene in hot water, whilst in the presence of cold water the yield declined to 70 per cent. (T., 1911, **99**, 2072).

When the reaction between bromine water and indene was submitted to a careful quantitative examination, according to the general method described in previous communications, considerable difficulty was experienced in obtaining trustworthy data at the lower temperatures owing to the formation of pasty aggregates consisting of the reaction products mixed with unchanged indene. On overcoming this difficulty by the addition of kieselguhr to the reaction mixture, a practically quantitative conversion of indene to the bromohydrin

occurred at the ordinary temperature, and no appreciable difference was observed when the reaction was carried out at 90°. The discrepancy to which reference has been made is thus to be ascribed to incomplete reaction, caused by defective admixture at the lower temperature, and the conclusion is reached that the reaction between bromine water and indene is not appreciably affected by raising the temperature to 90°. In view of the sensitiveness to heat and light of dilute aqueous solutions of hypobromous acid, it is very remarkable that bromine water when functioning as a source of potential hypobromous acid should be capable of exhibiting such indifference to either of these influences. That the reaction involves an intermediate formation of dibromide is unlikely, considering the resistance of dibromohydrindene to partial hydrolysis (*v. supra*).

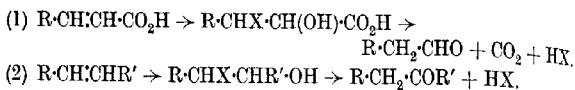
Owing, first, to the common instability of halogenohydrins in contact with hot dilute acid, and, secondly, to the oxidative action of warm aqueous solutions of chlorine and bromine, considerable difficulty exists in studying the addition of hypochlorous and hypobromous acids to unsaturated substances by the use of hot chlorine water or bromine water; it is hoped, however, to investigate other instances in which the halogenohydrin, like the bromohydrin of indene, is stable under the conditions mentioned. The evidence now available leads to the suggestion that even at high temperatures and in the presence of sunlight the velocity of halogenohydrin formation is much greater than the velocity of decomposition of hypochlorous or hypobromous acid. The complete scheme of reaction for indene and bromine water is summarised in the appended diagram, the only processes which occur to any appreciable extent being indicated by the thick arrows:



Preliminary attempts to utilise chlorine water as a source of potential hypochlorous acid in a similar reaction were unsuccessful, owing to the ready conversion of indene to tarry matter under the conditions adopted. It is of interest, however, that indene combines readily with hypochlorous acid, a 77 per cent. yield of chlorohydroxyhydrindene having been obtained by this method (Weissgerber, *Ber.*, 1911, 44, 1443).

Attention has already been directed (T., 1921, 119, 1775) to the very convenient method which is available for the preparation, in excellent yield, of phenylacetaldehyde from cinnamic acid by the successive action of chlorine water and aqueous alkali and acid. In a like manner,  $\beta$ -hydrindone is easily accessible from indene by suc-

cessive treatment with bromine water, alcoholic alkali, and dilute acid. The two general methods involved in these operations are summarised in the following schemes of reaction:



Heusler and Schieffer (*Ber.*, 1899, **32**, 30) have directed attention to the very reactive nature of the halogen in chlorohydroxyhydrindene, the monomethyl ether of hydrindeneglycol being produced by warming the substance with alcoholic sodium methoxide; in the case of bromohydroxyhydrindene the corresponding monoethyl ether was produced on treatment with warm alcoholic sodium ethoxide, and this derivative underwent hydrolysis with hot dilute sulphuric acid, yielding  $\beta$ -hydrindone. The final treatment with acid was found to be desirable even when the hydrolysis was effected by means of a slight excess of alcoholic potassium hydroxide.

#### EXPERIMENTAL.

*The Interaction between Cold Bromine Water and Indene.*—(1) Indene was added in portions of 5 grams to 1000 c.c. of water, the mixture being cooled to about  $2^\circ$  and submitted to vigorous mechanical stirring throughout the experiment. A slow current of air charged with bromine vapour was passed into the liquid until the attainment of a permanent pale yellow tint, whereupon a titrimetric estimation was made of the amount of hydrobromic acid contained in an aliquot part of the aqueous liquid, in accordance with the principle outlined in previous communications. The process was repeated until 20 grams of indene had been added, the progress of the reaction being ascertained by titration at the end of each stage. Towards the end of the experiment the absorption of bromine was slow, owing to the formation of a pasty mass containing unchanged indene. The titration values fluctuated considerably, and indicated yields of bromohydrin varying from 50 to 70 per cent. of the amounts theoretically possible. By washing the pasty product with light petroleum, the solid bromohydrin was obtained in an almost pure condition; after two recrystallisations from methylated spirit, it melted at  $130^\circ$  (Found: Br = 37.7.  $\text{C}_9\text{H}_9\text{OBr}$  requires Br = 37.5 per cent.). The petroleum washings contained unchanged indene together with a heavy oil, which was reserved for further examination.

(2) A similar experiment was carried out with the addition of light petroleum, the titration values being corrected in accordance with the results of a control experiment which indicated a slight

absorption of bromine by the petroleum under the experimental conditions. The formation of a semi-solid mass was prevented by the petroleum, and the titration results corresponded with yields of bromohydrin varying from 75 to 85 per cent. of the amounts theoretically possible. The petroleum, on evaporation, yielded a small quantity of a heavy oil; this contained dibromohydrindene, which was probably formed largely as a result of reaction in the petroleum phase.

(3) The experiment was repeated, with the substitution of kieselguhr (10 grams) for light petroleum. Ready absorption of bromine occurred, and the titrimetric estimations indicated an almost complete conversion of indene to bromohydrin, the mean value being 98 per cent. The actual weight of the solid product collected was about 90 per cent. of the theoretical yield.

*The Interaction between Bromine Water and Indene at 90°.*—Six distinct experiments were performed, each dealing with a different concentration of indene, the procedure being in each instance as follows:

To 1000 c.c. of water, maintained at 90°, was added in one portion a known weight of indene (5, 10, 15, 20, 30, and 40 grams). To the mixture, thoroughly emulsified by vigorous shaking, a 7 per cent. solution of bromine in aqueous potassium bromide was added with moderate rapidity until the attainment, after continued shaking, of a permanent pale yellow tint. A considerable quantity of the resulting bromohydrin remained in solution at 90°, and crystallised in long, colourless needles on cooling; the remainder of the solid product formed hard but somewhat sticky aggregates. The aqueous filtrate and washings were freed from traces of bromine by the passage of a rapid air current, after which an aliquot portion was titrated with standard sodium bicarbonate solution. The yields of bromohydrin corresponding with the titration results varied from 98.5 to 100 per cent. of the amounts theoretically possible, the mean value being 99 per cent.

A preliminary control experiment showed that the amount of hydrobromic acid formed, in the absence of indene, under the conditions adopted was so small as to be negligible. That the high titration values were not due to decomposition of hypobromous acid or hydrolysis of the bromohydrin is also evident from the fact that between 90 and 95 per cent. of the calculated yield of the solid compound was actually collected in the six experiments described.

*Subsidiary Products of the Reaction.*—The various preparations of bromohydroxyhydrindene were united (480 grams) and recrystallised carefully, in an attempt to isolate the second externally



compensated form of the substance which is theoretically possible. The main product of the reaction, after recrystallisation from alcohol, melted at  $130^{\circ}$ , and the final mother-liquors yielded a small amount of an oil, the bulk of which distilled at  $130\text{--}165^{\circ}/18$  mm. (34 grams). The distillate contained 39.8 per cent. of combined bromine, and appeared to consist essentially of bromohydroxyhydrindene ( $\text{C}_9\text{H}_9\text{OBr}$  requires  $\text{Br} = 37.5$  per cent.). After keeping for several weeks, the oil, which possessed a very irritating odour, deposited crystals; these, when separated from adhering mother-liquor, showed an ill-defined melting point, pronounced softening occurring at about  $85^{\circ}$ . The material was extremely soluble in most of the usual organic solvents, from which it was deposited as an oil. The evidence thus appears to indicate the formation of a small amount of an isomeric bromohydrin of low melting point and high solubility. Similar observations have been recorded in the cinnamic acid series (*loc. cit.*, p. 1776).

The light petroleum washings of the original semi-solid separations also yielded a similar oily product, the major portion of which distilled at  $135\text{--}160^{\circ}/18$  mm. The percentage of bromine (49.1) corresponded in this instance with a mixture of dibromide and bromohydrin.

*The Conversion of Bromohydroxyhydrindene to  $\beta$ -Hydrindone.*—Bromohydroxyhydrindene was heated under reflux for half an hour with a 4 per cent. alcoholic solution of potassium hydroxide (slightly more than one equiv.). The bulk of the alcohol was then removed and the residue again heated under reflux with an excess of dilute sulphuric acid. On steam distilling the product, the ketone was readily obtained as a colourless, crystalline mass, in about 75 per cent. yield. It separated from dilute alcohol in long, silky needles having a very faint yellow tinge. After several weeks, the crystals became yellow and somewhat pasty. The melting point of the freshly recrystallised substance was  $58^{\circ}$ ; this result agrees with the observations of Schad (*Ber.*, 1893, 26, 222) and Heusler and Schieffer (*loc. cit.*), the value  $61^{\circ}$  recorded by Benedict and Wislicenus (*Annalen*, 1893, 275, 352) being doubtlessly too high.

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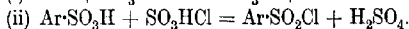
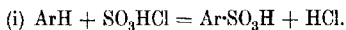
[Received, September 1st, 1922.]

CCCVI.—*Aromatic Sulphonyl Chlorides.*

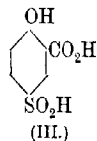
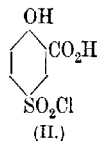
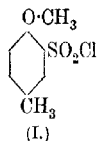
By JESSIE STEWART.

DURING an investigation of certain properties of aromatic disulphides some difficulty was met in obtaining these substances in a pure condition and in sufficient quantity. Undoubtedly the best method of preparation is by reduction of the corresponding sulphonyl chlorides, but the usual method of obtaining these substances from the sulphonates by interaction with phosphorus pentachloride is somewhat troublesome when applied to large quantities and does not always yield a pure product, whilst thionyl chloride, which in some cases gives excellent yields of pure material, is not always applicable. Other drawbacks to the use of phosphorus pentachloride are illustrated by the case of *m*-sulphobenzoic acid. This yields the dichloride, which requires partial hydrolysis before reduction to the thiol derivative can be advantageously effected. In this case it was found (T., 1921, **119**, 1792) that the required chlorosulphonyl derivative could be readily obtained from benzoic acid by reaction with chlorosulphonic acid. It therefore seemed desirable to apply this process to other disulphides and sulphinic acids which were required. Several cases of the use of chlorosulphonic acid in preparing aromatic sulphonyl chlorides are recorded in literature; in some of these the isolated sulphonate or sulphonic acid was treated with the reagent, whilst in others the sulphonyl chloride was directly obtained by reaction of the aromatic compound with chlorosulphonic acid. Without attempting quite completely to enumerate the cases recorded, the following may be mentioned to illustrate the scope of the material submitted to this reagent. Thus benzenesulphonyl chloride (*Ber.*, 1909, **42**, 1802, 2057), the toluenesulphonyl chlorides (Harding, T., 1921, **119**, 1261), *m*-nitrobenzenesulphonyl chloride (D.R.-P. 89997, 1896), *o*-nitrophenol-*p*-sulphonyl chloride (*Z. angew. Chem.*, 1920, **33**, 8), tetrahydronaphthalenesulphonyl chloride (D.R.-P. 336615, 1921), and veratrolesulphonyl chloride (Brown and Robinson, T., 1917, **111**, 953) have been obtained by this process and except in the case of benzenesulphonyl chloride the yield and quality of the product appear to have been excellent. These isolated examples seemed to indicate the possibility of a more general application of the reagent. The experiments now described were undertaken for the purpose of this extension, with the ultimate object of finding satisfactory methods for the preparation of disulphides and sulphinic acids which are otherwise not easily obtained in quantity. In the majority of the cases studied, the results have been entirely satisfactory.

The mechanism of the formation of the sulphonyl chlorides by this method has been fully discussed by Harding (*loc. cit.*) in the case of the toluene derivatives; the observations made in the progress of the experiments now described support his conclusion that these substances are formed in a secondary reaction of the sulphonie acid with excess of chlorosulphonic acid, the complete process being represented as follows:

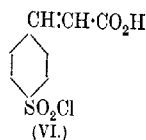
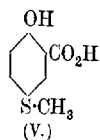
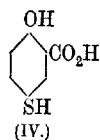


In the experimental part of this paper the preparation of sulphonyl chlorides from *p*-dichlorobenzene, acetanilide, salicylic acid, *p*-tolyl methyl ether, cinnamic acid, and phenylacetic acid is described. In the case of *p*-dichlorobenzene the constitution of the sulphonyl chloride and of the corresponding disulphide is evident. The derivative obtained from acetanilide was the *p*-sulphonyl chloride, for the substance was identical with that obtained by the action of phosphorus pentachloride on sodium acetanilide-*p*-sulphonate (Schroeter, *Ber.*, 1899, **39**, 1566) and yielded on reduction the characteristic 4:4'-dithioacetanilide, which exists in two isomeric forms (Hinsberg, *Ber.*, 1906, **39**, 2429); both these were isolated.



*p*-Tolyl methyl ether yielded a sulphonyl chloride of the constitution (I); this follows from the facts that it is identical with the substance obtained from the sulphonie acid of the given structure and yields a sulphonie acid which is the same as that obtained from the amino-derivative by Gattermann's method (*Ber.*, 1899, **39**, 1139). The structure of the sulphonyl chloride yielded by salicylic acid was also determined. As might be expected, it is identical with the chloride obtained from sulphosalicylic acid, but the structure of the latter seems by no means firmly established. The method planned by Hirsch (*Ber.*, 1900, **33**, 3238) for determining the orientation of the sulphonie group was not successful, but the substance is commonly referred to in literature as 5-sulphosalicylic acid. There is no reason to doubt this structure and it has now been proved to be correct, for the sulphinic acid (III) obtained from 5-aminosalicylic acid by Gattermann's process is identical with that formed from the chlorosulphonylsalicylic acid (II) by reduction with sodium sulphite. The corresponding disulphide is readily obtained

from the sulphonyl chloride by the usual methods. It has been stated that a substance of this character is formed by interaction of sulphur chloride and salicylic acid (D.R.-P. 46413, 1888), but the product of this reaction is amorphous and appears not to be the same as the 5:5'-disulphide now obtained. It is worthy of notice that this disulphide, like *m*-dithiobenzoic acid (T., 1921, 119, 1793), is resolved by aqueous alkali hydroxide, giving the mercaptan (IV). The alkaline solution, when treated with methyl sulphate, yields 5-methylthiolsalicylic acid (V).



Cinnamic acid yields the *p*-chlorosulphonyl derivative (VI); this was identified by oxidation of the corresponding sulphonamide, when *p*-sulphaminobenzoic acid was obtained. Search for the *o*-chlorosulphonyl derivative in the product was made by reduction to the thiol. Friedländer has shown (*Ber.*, 1913, 46, 1903) that thionaphthen is readily formed from *o*-thioleinnamic acid by oxidation with alkaline ferrieyanide; and since this substance is very easily detected, the reaction was applied to the crude thiol obtained by reduction of the chlorosulphonyl compound, but no thionaphthen was encountered. It is therefore evident that the *o*-sulphonyl chloride is not formed to any appreciable extent during the process of sulphonation under the conditions adopted. Phenylacetic acid is readily attacked by cold chlorosulphonic acid, but the isolation of the chlorosulphonyl derivative proved difficult, since the substance is somewhat easily attacked by ice-cold water. There is little doubt that the least soluble portion of the product is the para-derivative; but the quantity available was not sufficient to permit this to be determined or to allow investigation of the more soluble portion. The few examples now described together with those previously recorded are sufficient to show the advantage of the method; more recent experiments have shown that it may be applied to derivatives of acetanilide, from which the aminosulphinic acids and the disulphides may thus be satisfactorily obtained.

#### EXPERIMENTAL.

2:5-Dichlorobenzenesulphonyl chloride,  $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{SO}_2\text{Cl}$ .—A mixture of *p*-dichlorobenzene with chlorosulphonic acid (5 mols.) was heated at 150° for one hour. The cooled liquid was poured over crushed ice, when the required chlorosulphonyl derivative separated in the

solid state. The yield of crude material was 85 per cent. of that required by theory. After recrystallisation from cold alcohol, the substance was obtained in colourless needles which melted at  $39^{\circ}$  (Found: S = 13.0; Cl = 43.2. Calc., S = 13.0; Cl = 43.4 per cent.). The corresponding amide, prepared in the usual manner, melted, after recrystallisation from hot water, at  $181^{\circ}$ ; Holleman (*Rec. trav. chim.*, 1911, **30**, 331) gives m. p.  $185-186^{\circ}$ .

2 : 5 : 2' : 5'-Tetrachlorodiphenyl disulphide was prepared by reduction of the chloride with zinc dust in boiling acetic and hydrochloric acids. After three hours, the filtered liquid was cooled, the zinc derivative of the mercaptan which was then precipitated was collected and decomposed with a mixture of alcohol and hydrochloric acid, and ferric chloride added, the required disulphide being obtained in the crystalline state. The substance separated from warm alcohol in colourless needles which melted at  $81-82^{\circ}$  (Found: C = 40.1; H = 1.9; S = 18.0. Calc., C = 40.4; H = 1.7; S = 17.97 per cent.).

Acetanilide-*p*-sulphonyl Chloride,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ .—A solution of acetanilide in chlorosulphonic acid (5 mols.) was kept at  $60^{\circ}$  for two hours. The crude product, which formed about 85 per cent. of the theoretical amount, was isolated in the usual manner. After recrystallisation from benzene, it was obtained in colourless needles which melted at  $149^{\circ}$  (Found: Cl = 15.1; S = 13.9; N = 6.0. Calc., Cl = 15.2; S = 13.7; N = 6.0 per cent.). When this substance was treated with zinc dust in boiling acetic acid the zinc derivative of 4-thiolacetanilide was obtained, from which the corresponding 4 : 4'-dithioacetanilide was prepared in the usual manner. This substance melted at  $182^{\circ}$  (Found: S = 19.2; N = 8.7. Calc., S = 19.3; N = 8.4 per cent.) and was evidently the  $\alpha$ -isomeride; when it was kept at the atmospheric temperature, the  $\beta$ -isomeride of melting point  $213-214^{\circ}$  was formed (compare Hinsberg, *loc. cit.*).

3-Chlorosulphonyl-*p*-tolyl Methyl Ether (I).—One volume of *p*-tolyl methyl ether was slowly added to chlorosulphonic acid (5 vols.) at  $0^{\circ}$ , and the solution poured over crushed ice, when an almost theoretical yield of the required chlorosulphonyl derivative separated in the solid condition. When dry, the crude material melted at  $79-81^{\circ}$ , and after recrystallisation from alcohol it was obtained in colourless needles which melted at  $84^{\circ}$  (Found: Cl = 15.9; S = 14.7. Calc., Cl = 16.1; S = 14.5 per cent.). This material and the amide prepared from it (m. p.  $183^{\circ}$ ) were identical with the corresponding substances prepared from 3-sulpho-*p*-tolyl methyl ether.

4 : 4'-Dimethoxydi-*m*-tolyl Disulphide,  $(\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me})_2\text{S}_2$ .—The

corresponding mercaptan, which was prepared by reduction of the chlorosulphonyl derivative, was oxidised by treatment with ferric chloride. The disulphide, after recrystallisation from alcohol, was obtained in pale yellow prisms which melted at  $67^{\circ}$  (Found: C = 62.3; H = 6.1; S = 21.3.  $C_{10}H_{18}O_2S_2$  requires C = 62.7; H = 5.9; S = 20.9 per cent.).

*5-Chlorosulphonylsalicylic Acid (II).*—Salicylic acid was gradually added to cooled chlorosulphonic acid (5 mols.), the solution kept at  $75^{\circ}$  for one hour, and the solid chlorosulphonyl derivative isolated in the usual manner, particular care being taken to avoid rise of temperature during the decomposition with ice and to remove the material from contact with water as soon as possible. With these precautions, the yield was about 60 per cent. of the theoretical, but otherwise considerable loss may arise from hydrolysis of the product. 5-Chlorosulphonylsalicylic acid separates from benzene in colourless prisms which melt at  $169$ – $171^{\circ}$  (Found: Cl = 14.8; S = 13.8. Calc., Cl = 15.0; S = 13.5 per cent.). The same substance was readily obtained from sulphosalicylic acid by treatment with chlorosulphonic acid.

*5-Sulphinosalicylic acid (III)* was prepared by two methods. 5-Aminosalicylic acid was converted in aqueous solution to the corresponding diazonium derivative. This was treated with an excess of sulphurous acid in presence of copper powder, the latter removed, and the required sulphinic acid extracted from the aqueous solution with ether. After purification, the product melted at  $159^{\circ}$  and was identical with that obtained by reduction of the chlorosulphonyl derivative. The yields of sulphinic acid from this process were very poor; but the substance is easily obtained by the following process.

Five grams of chlorosulphonylsalicylic acid were gradually added with shaking to an aqueous solution of 20 grams of sodium sulphite, sodium hydroxide being added, if necessary, to maintain alkalinity. Subsequently excess of dilute sulphuric acid was added and the liberated sulphinic acid removed by solution in ether. The yield of crude material was 3.6 grams. The substance was purified by recrystallisation from ether, when it was obtained in colourless needles which melted at  $159^{\circ}$  (Found: C = 41.4; H = 3.1; S = 15.9. Calc., C = 41.6; H = 3.0; S = 15.8 per cent.). This sulphinic acid is readily soluble in cold water; when mixed with phenetole in sulphuric acid, it gave the characteristic blue solution.

*5:5'-Dithiosalicylic Acid.*—Thirty grams of zinc dust and 100 c.c. of concentrated hydrochloric acid were gradually added with shaking to an alcoholic solution of 20 grams of 5-chlorosulphonylsalicylic acid. When reduction was complete, the excess of zinc

dust was removed and the clear liquid treated with solid ferric chloride, care being taken that sufficient hydrochloric acid was present to prevent the formation of the purple iron salt. Partial separation of the required disulphide took place immediately, but this was completed by the careful addition of water. The yield of the crude material was about 78 per cent. of the theoretical. To purify the product, it was first treated with aqueous sodium carbonate, when some ester which had been formed during the treatment in alcohol remained insoluble. The disulphide was recovered from the solution and then recrystallised from a mixture of alcohol and water, when it was obtained as a pale yellow, crystalline powder, which melted at  $236^{\circ}$  (Found: C = 49.4; H = 3.2; S = 18.8. Calc., C = 49.7; H = 3.0; S = 18.9 per cent.).

5-Thiolsalicylic acid (IV) was prepared by reduction of the disulphide with glucose according to the method of Claasz (*Ber.*, 1912, 45, 2424). The mercaptan was set free from the alkaline mixture with dilute sulphuric acid and recrystallised from hot water. It formed small, pale yellow needles which melted at  $150$ – $152^{\circ}$  and were converted to the disulphide by mild oxidising agents. The same substance may be prepared by hydrolysis of the disulphide with alkali hydroxide. The latter substance was treated with boiling N-sodium hydroxide (8 mols.) for half an hour; the mercaptan was precipitated in the crystalline state when excess of dilute sulphuric acid was added to the alkaline solution.

5-Methylthiolsalicylic Acid (V).—A solution of 10 grams of the disulphide in excess of N-sodium hydroxide was boiled for half an hour, cooled, and shaken with 6 c.c. of methyl sulphate. On adding excess of mineral acid to the clear solution, 7.2 grams of 5-methylthiolsalicylic acid were liberated. This was recrystallised from hot water and thus obtained as a pale buff, crystalline powder which melted at  $126^{\circ}$  (Found: C = 52.3; H = 4.2; S = 17.7. Calc., C = 52.2; H = 4.3; S = 17.4 per cent.). It is evident that the methylthiol group is present in this substance, since it was not converted to a disulphide by ferric chloride. Moreover, methylation of the hydroxyl under these conditions can scarcely be expected when the difficulty experienced by Graebe (*Annalen*, 1905, 340, 204) in methylating salicylic acid is recalled.

4-Chlorosulphonylcinnamic Acid (VI).—A solution of cinnamic acid in chlorosulphonic acid (about 8 mols.) was kept at  $50$ – $60^{\circ}$  for half an hour. The product was isolated in the usual manner and after recrystallisation from acetic acid 4-chlorosulphonylcinnamic acid was obtained in colourless needles which melted and decomposed at  $226^{\circ}$  (Found: Cl = 14.3; S = 12.8. Calc., Cl = 14.4; S = 13.0 per cent.). 4-Sulphaminocinnamic acid was obtained

in the usual manner from the chloride; it formed colourless prisms which decomposed between 250–260° according to the rate of heating (compare Palmer, *Amer. Chem. J.*, 1882, 4, 163) (Found: S = 14.1; N = 6.2. Calc., S = 14.1; N = 6.2 per cent.). This sulphonamide was oxidised by chromic acid in presence of warm dilute sulphuric acid. On cooling the reaction mixture after oxidation was complete, the product separated in the crystalline state. After being purified, the substance decomposed at about 280° (Found: S = 15.9; N = 7.1. Calc., S = 15.9; N = 6.9 per cent.). This behaviour agrees with that assigned to 4-sulphaminobenzoic acid by Palmer (*loc. cit.*); moreover, the meta-isomeride melts at 233°, whilst the ortho-derivative melts indefinitely at a lower temperature than either of these and loses water.

*Chlorosulphonylphenylacetic Acid*,  $\text{HO}_2\text{C}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ .—Phenylacetic acid was gradually added to cooled chlorosulphonic acid (5 mols.). Reaction was immediate and after the lapse of a few minutes the solution was poured over crushed ice and the solid product isolated from moisture as rapidly as possible. The maximum yield obtained was about 35 per cent. of the theoretical. After recrystallisation from benzene, in which it was readily soluble, the chlorosulphonyl derivative was obtained in colourless prisms which melted at 136° (Found: Cl = 15.1; S = 13.6. Calc., Cl = 15.1; S = 13.6 per cent.). The corresponding amide is readily soluble in water; it separates from this solvent in shining plates which melt at 176°.

I wish to express my thanks to Professor Smiles for his advice and for the interest he has taken in the work recorded above.

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CCCVII.—*Limits for the Propagation of Flame in Vapour-Air Mixtures. Part II. Mixtures of More than One Vapour and Air at the Ordinary Temperature and Pressure.*

By ALBERT GREVILLE WHITE.

IN a limit mixture, the heat given out by the burning gas mixture is sufficient, and only just sufficient, to enable propagation of flame to take place. At first sight, it would thus appear reasonable to assume that when two or more limit mixtures containing different combustibles are mixed, the mixture obtained would always be a



limit mixture—always assuming that the limit mixtures used are all similar, that is, all lower- or all upper-limit mixtures. If  $n_1, n_2, n_3, \dots$  are the percentages of different combustibles found in the final limit mixture, and  $N_1, N_2, N_3, \dots$  are the percentages of the same combustibles required to give limit mixtures when each is mixed with air separately, then the volume of the final mixture is given by the sum of a series of terms  $100n_1/N_1, 100n_2/N_2, 100n_3/N_3, \dots$  and is equal to 100. We thus see that  $n_1/N_1 + n_2/N_2 + n_3/N_3 + \dots = 1$ .

This is a generalised form of the formula connecting the limits for the propagation of flame in combustible gas-air mixtures originally put forward by Le Chatelier for binary mixtures. Given the limits of the combustibles taken separately, it fixes the limit for any mixture of these in known proportions, or the amount of any one combustible necessary to give a limit mixture with known quantities of the others and of air. The formula has been verified experimentally by Le Chatelier (*Ann. Mines*, 1891, [viii], 19, 388), Le Chatelier and Boudouard (*Compt. rend.*, 1898, 126, 1344), Eitner (*Habilitationschrift*, München, 1902), and Coward and Brinsley (T., 1919, 115, 27).

These investigators used mixtures of permanent gases, chiefly hydrogen, carbon monoxide, methane, and coal gas. The results obtained agreed fairly closely with those calculated from the formula, but the number of experiments was small except in the case of Coward and Brinsley. These authors state that the discrepancies found by them, although small, are greater than could be accounted for by experimental error. Payman (T., 1919, 115, 1436), using mixtures of methane with atmospheres containing varying amounts of oxygen, has shown that the addition rule underlying Le Chatelier's formula seems to hold for a large portion of the range over which he worked. White and Price (T., 1919, 115, 1462), using mixtures of ether with acetone and alcohol, decided that the mixture law was followed by these vapours except for upward and horizontal propagation at the upper limit, when large discrepancies were found. Recently, Boussu (*Compt. rend.*, 1922, 175, 30) has determined the lower limit for the propagation of flame in various mixtures of alcohol, petrol, and ether in air. He drew the conclusion that the mixture law was obeyed within the limits of experimental error, but the differences between the calculated and experimental values were sometimes more than 5 per cent.

#### EXPERIMENTAL.

During the present work the limit determinations were carried out as described in the first part of this research (this vol., p. 124).

TABLE I.

Showing the ranges that propagate flame in benzene-toluene-air and acetone-methyl ethyl ketone-air mixtures.

All calculations were based on the formula given on p. 2562.

Original temperature of mixture.	Composition of combustible in mixture by vol.		Upward propagation.		Horizontal propagation.		Downward propagation.	
	% Benzene.	% Toluene.	Range found.	Range calc.	Range found.	Range calc.	Range found.	Range calc.
Lower limits at 18±3°	0	100	1.31	—	1.30	—	1.32	—
			to		to		to	
			6.75		5.80		4.60	
Upper limits at 60°	25	75	1.32	1.34	1.33	1.34	1.35	1.36
			to	to	to	to	to	to
			6.95	6.90	5.95	6.00	4.80	4.80
	50	50	1.37	1.38	1.38	1.38	1.39	1.39
			to	to	to	to	to	to
			7.05	7.10	6.25	6.20	5.05	5.03
	75	25	1.41	1.41	1.40	1.42	1.43	1.43
			to	to	to	to	to	to
			7.15	7.25	6.30	6.40	5.30	5.28
	100	0	1.45	—	1.46	—	1.47	—
			to		to		to	
			7.45		6.65		5.55	
		% Methyl ethyl ketone.						
		% Acetone.						
17±3°	0	100	2.05	—	2.05	—	2.10	—
			to		to		to	
			9.9		8.5		7.4	
	33	67	2.31	2.27	2.32	2.28	2.37	2.33
			to	to	to	to	to	to
			11.0	10.65	9.00	8.90	7.70	7.70
	67	33	2.58	2.53	2.63	2.58	2.66	2.62
			to	to	to	to	to	to
			12.0	11.55	9.50	9.40	7.95	8.05
	100	0	2.90	—	2.96	—	2.99	—
			to		to		to	
			12.6		9.90		8.40	

except that dried air was used only for mixtures containing either alcohol or acetone. The two liquids to be used were weighed out into a well-stoppered bottle in the required proportions, and this mixture was then utilised for filling the tubes. Mixtures were never kept for any length of time before use. It was considered necessary to test binary mixtures only, as if the mixture law holds for all pairs of vapours, it presumably holds for complex mixtures.

Four series of experiments were carried out, the first of these dealing with two pairs of vapours of which the limits did not appear to be much affected by cool flame phenomena. In the second series, at least one vapour of the pairs examined possessed a distinct cool flame. The third series was intended to test further

the applicability of Le Chatelier's rule to lower limits, whilst the fourth consisted of experiments on pairs of vapours of which one was carbon disulphide.

All limits were determined in tubes 5 cm. in diameter and 1.5 metres long.

#### *Results.—Series A.*

The results obtained for the first series are shown in Table I.

As the accuracy aimed at in these experiments was of the order of 1 per cent., it will be seen that the deviations from Le Chatelier's rule are generally of much the same order as the experimental error. A definite exception occurs for upward propagation at the upper limit in the mixtures containing the two ketones. For both of the mixtures examined, the value found is very definitely higher than that calculated. This deviation could almost have been predicted from the behaviour of acetone in tubes of different diameters described in a previous communication (*loc. cit.*). It was there shown that the limit for upward propagation at the upper limit in the tubes used was greatest in a 2.5-cm. tube (12.95 per cent.), and least in a 7.5-cm. tube (11.80 per cent.), a result attributed to the relative instability of the appropriate flame in the larger tubes. This assumption appears to receive some confirmation from the present results. Le Chatelier's rule being assumed to hold, calculation from the limit result for the mixture richer in acetone gives the limit for pure acetone in a 5-cm. tube as 13.4 per cent. The remarks previously made regarding the ignition of upper-limit mixtures of acetone in air for upward and horizontal propagation apply equally to corresponding mixtures of the two ketones in air.

#### *Series B.*

The limits for the propagation of flame determined for this series are shown in Tables II, III, and IV.

No attempt was made to find out if any middle limit existed in the case of ether-acetaldehyde-air mixtures.

Consistent results for the upper limit for horizontal and upward propagation were only obtained with great difficulty over a good deal of the ether-alcohol and ether-acetone-air ranges, and the figures given are certainly less accurate than those determined for the pure solvents.

Owing to the intervention of the cool flame the results given in Tables II and III sometimes differ from those found by White and Price. The same conclusions can be drawn from both sets, however. Le Chatelier's rule appears to be followed very well for lower limits and for upper limits for downward propagation. For

TABLE II.

Showing the ranges that propagate flame in ethyl ether-acetone-air mixtures. Temperature  $17 \pm 3^\circ$ .

All calculations are based on the formula given on p. 2562.

Composition of combustible in mixture by vol.		Upward propagation.		Horizontal propagation.		Downward propagation.	
% Ether.	% Acetone.	Range found.	Range calc.	Range found.	Range calc.	Range found.	Range calc.
0	100	2.90 to 12.6	—	2.96 to 9.9	—	2.99 to 8.4	—
25	75	2.56 to 11.2	2.53 to 15.5	2.62 to 10.5	2.59 to 12.0	2.65 to 7.75	2.62 to 7.74
40	60	No cool flame					
45	55	— and 20 to 27					
50	50	2.27 to 12.3 and — to —	2.25 to 20.0	2.28 to 10.1	2.30 to 15.0	2.33 to 7.20	2.32 to 7.17
55	45	No middle limit					
60	40	— to 38. No middle limit		No cool flame			
65	35						
66	34			— and 17 to 25			
75	25	2.06 to 41	2.03 to 28	2.08 to 10.4 and 14 to 27	2.07 to 21.0	2.10 to 6.65	2.09 to 6.68
80	20			— to 9.3 and 14 to 28			
90	10			— to 8.65 and 10.0 to —			
92.5	7.5			No middle limit			
100	0	1.84 to 48	—	1.88 to 33	—	1.90 to 6.25	—

propagation upwards and horizontally, however, the calculated results are almost invariably far from the mark, and any agreement appears to be purely accidental. This appears to be due to the fact that one of the two combustibles is capable of burning with a cool flame. Agreement is far from satisfactory, however, when both combustibles give a cool flame, as can be seen from Table IV. The best idea of the results is obtained from Figs. 1 and 2, in which the propagation ranges are shown graphically for different proportions of pairs of combustibles.

TABLE III.

Showing the ranges that propagate flame in ethyl ether-ethyl alcohol-air mixtures.

All calculations are based on the formula given on p. 2562.

Original temperature of mixture.	Composition of combustible in mixture by vol.		Upward propagation.		Horizontal propagation.		Downward propagation.	
	Ether.	Acetone.	Range found.	Range calc.	Range found.	Range calc.	Range found.	Range calc.
Lower limits	0	100	3.69	—	3.75	—	3.78	—
at $18 \pm 3^\circ$			to 18.0		to 13.8		to 11.5	
Upper limits	25	75	2.96	2.95	2.98	3.00	3.05	3.03
at $60^\circ$			to 16.3	to 21.5	to 11.4	to 16.5	to 9.6	to 9.67
	50	50	2.48	2.45	2.50	2.50	2.51	2.53
			to 13.6	to 27.5	to 9.8	to 20.5	to 8.20	to 8.35
A	60	40	2.30	—	—	—	2.37	—
			to 13.5				to —	
	65	35	— to 24					
	70	30	— to 34					
	75	25	2.10	2.10	2.13	2.15	2.16	2.17
			to 37	to 37	to 10.1	to 27.5	to 7.20	to 7.35
	80	20			No cool flame			
	85	15			— to 9.6 and 16.5 to 23			
$19 \pm 2^\circ$	90	10			— to 30. No middle limit			
	100	0	1.84	—	1.88	—	1.90	—
			to 48		to 33		to 6.25	
As above at A	100	0	1.84	—	1.88	—	1.90	—
			to 58		to 41		to 6.55	

TABLE IV.

Showing the ranges for the propagation of flame in ethyl ether-acetaldehyde-air mixtures. Temperature  $18 \pm 2^\circ$ .

All calculations are based on the formula given on p. 2562.

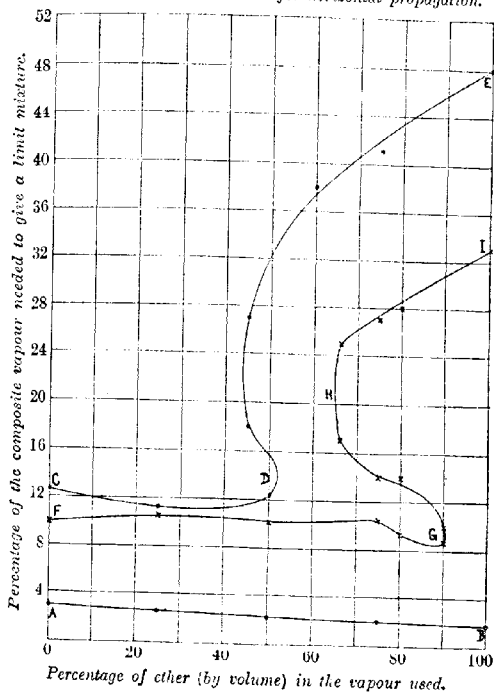
Original temperature of mixture.	Composition of combustible by vol. in mixture.		Upward propagation.		Downward propagation.	
	Ether.	Acetaldehyde.	Range found.	Range calc.	Range found.	Range calc.
	0	100	4.21 to 57	—	4.36 to 12.8	—
	25	75	3.20 to 47	3.18 to 54	3.31 to 10.1	3.29 to 10.1
	50	50	2.59 to 44	2.56 to 52	2.66 to 8.55	2.65 to 8.40
	75	25	2.15 to 46	2.14 to 50	2.20 to 7.20	2.21 to 7.20
	100	0	1.84 to 48	—	1.90 to 6.25	—

Fig. 1 shows the ranges that propagate flame in various ether-acetone-air mixtures. Flame is propagated upwards through all mixtures lying between the lines *AB* and *CDE*, and horizontally through those between *AB* and *FGHI*. The irregular form of the two upper lines is to be attributed to the two different types of

FIG. 1.

Showing the ether-acetone-air mixtures that propagate flame at  $18 \pm 3^\circ$ .

*AB* Lower limits.  
*CDE* Limits other than lower for upward propagation.  
*FGHI* Limits other than lower for horizontal propagation.



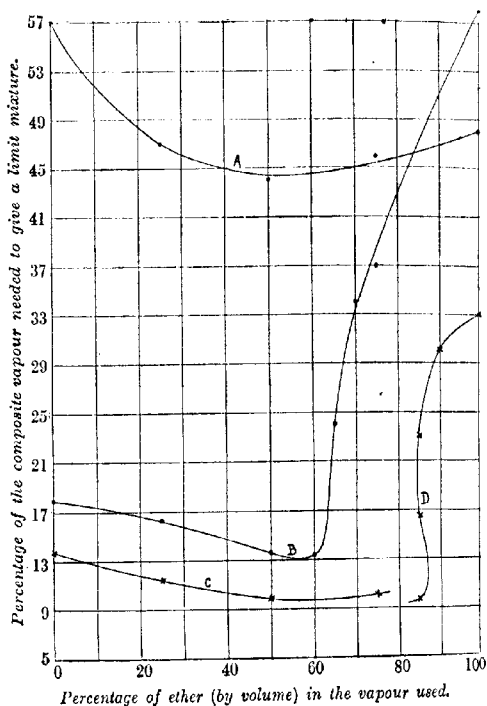
flame which function, cool to the ether side, but only slightly modified from the normal for mixtures containing much acetone. The latter flame corresponds to the roughly horizontal portions, *CD* and *FG*, *DE* and *GHI* being lines near which the flame is cool. The normal flame results seem to indicate that without the cool flame the ether upper limits for horizontal and upward propagation would be lower than those of acetone, as would be expected from

the calorific values of these two substances. This conclusion is supported by the ether-alcohol curves of Fig. 2. The determination of two portions of the curve for horizontal propagation in this figure at different temperatures was made for convenience.

FIG. 2.

Showing the limit mixtures (other than lower) that will propagate flame in ether-acetaldehyde-air and ether-ethyl alcohol-air mixtures.

- A Ether-acetaldehyde-air at  $18 \pm 2^\circ$  for upward propagation.
- B Ether-alcohol-air at  $60^\circ$  for upward propagation.
- C Ether-alcohol-air at  $60^\circ$  for horizontal propagation.
- D Ether-alcohol-air at  $19 \pm 2^\circ$  for horizontal propagation.



The author has previously shown (*loc. cit.*) that by using a narrower tube the horizontal propagation range of ether can be divided into two, (1) a cool range and (2) what may be termed a normal range. Figs. 1 and 2 show that this also occurs when the correct amount of a skitable combustible is added to the ether-air mixture. In the case of acetone, it has even been possible

to find two distinct ranges for upward propagation, the mixture required containing nearly equal volumes of the two vapours. It is thus evident that acetone and alcohol hinder the propagation of the cool flame, and the curves show that alcohol has a much greater effect than acetone. Fig. 2 shows that the propagation of the cool flame in either ether or acetaldehyde is hindered by the presence of the other, but the effect appears to be less marked than when acetone is added. Fig. 4 shows, however, that the addition of carbon disulphide to ether has a still smaller effect on the propagation of the cool flame.

*Series C.*

The results of the first two series showed that for the lower limit Le Chatelier's rule was closely followed by the five pairs of substances examined. To make the test more rigorous, five additional pairs of substances were utilised for further work involving only the lower limit. The mixtures used were methyl alcohol-ether, methyl alcohol-acetone, ethyl acetate-benzene, acetaldehyde-toluene, and ethyl nitrite-ether. To save space, the actual results are not given, but the agreement was little, if at all, inferior to that obtained with the first five pairs.

*Series D.*

The results of the first three series of experiments had shown that Le Chatelier's rule could generally be expected to hold for vapour-air mixtures, except when the cool flame entered. The cool flame differs from an ordinary flame in two respects—in the type of combustion occurring and the flame temperature, either of which might conceivably be the reason for its quasi-independent propagation. The flame temperature difference would appear to be the one which lends itself more easily to examination.

The author's work on the effect of temperature on the limits for the propagation of flame in ammonia-air (this vol., p. 1688), together with a consideration of similar results for methane-air, seemed to show that for these two gases, at the lower limit, at any rate, the propagation of flame depended on the attainment of a flame temperature peculiar to the gas under consideration. Should this effect be general, it might easily occur that a mixture of two vapours needing very different flame temperatures for propagation should have a propagation flame temperature approximating to that of the higher flame temperature over a portion of its range, whilst over most of the remainder only the vapour having the lower flame temperature would enter appreciably into the propagation of flame. The results of other workers previously cited seemed to show that mixtures of hydrogen with other gases



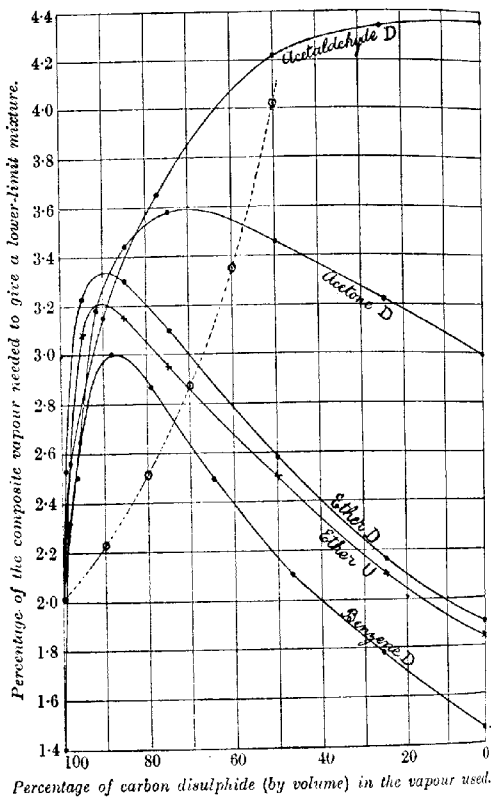
having propagation flame temperatures five or six hundred degrees higher obeyed Le Chatelier's rule fairly well. It was considered expedient, however, to examine mixtures of ether with carbon

FIG. 3.

Showing the lower limits for the propagation of flame in mixtures of carbon disulphide and certain other vapours with air.

D = downward propagation. U = upward propagation.

The dotted line passes through all mixtures containing 2.01% of carbon disulphide.



disulphide, the only one of the vapours previously examined by the author which gave a propagation flame temperature appreciably different from the normal. The results obtained were so interesting that the work was at once extended to mixtures of carbon disulphide

with benzene, acetone, and acetaldehyde. The results obtained are given in Tables V and VI, and are shown graphically in Figs. 3 and 4.

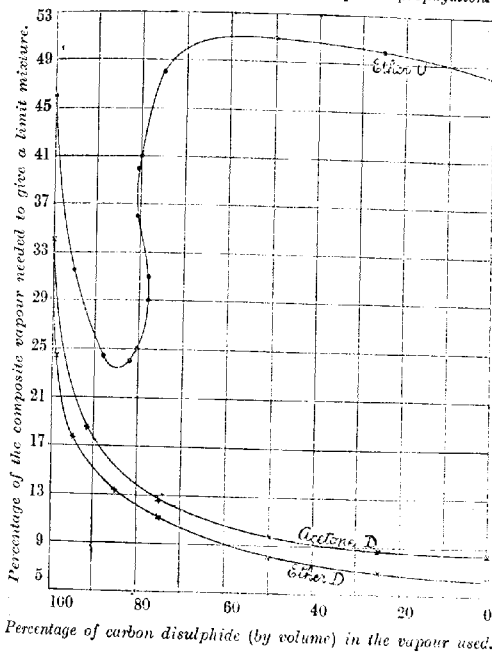
An examination of the two tables shows that the formula of Le Chatelier gives values far from those found experimentally, the partial agreement found over most of the range for upward

FIG. 4.

Showing certain limit mixtures (other than lower) for mixtures of carbon disulphide and air with ether and with acetone.

D = downward propagation.

U = upward propagation.



propagation at the upper limit in ether-carbon disulphide-air mixtures being obviously accidental.

In Table VII below are given the relative calorific values of the amounts of various vapour-air mixtures needed to enable propagation of flame to take place at the lower limit. Over a large portion of the range chosen, these values are approximately equal. The flame temperatures theoretically attained will thus be roughly equal for all these mixtures, so that the relation suggested above

TABLE V.

Showing the ranges that propagate flame in ethyl ether-carbon disulphide-air mixtures. Temperature  $17 \pm 3^\circ$ .

All calculations are based on the formula given on p. 2562.

Composition of combustible in mixture by vol.				Composition of combustible in mixture by vol.			
		Upward propagation.				Downward propagation.	
% Ether.	% Carbon disulphide.	Range found.	Range calc.	% Ether.	% Carbon disulphide.	Range found.	Range calc.
0	100	1.40 to 46	—	0	100	2.01 to 34	—
1	99	2.28 to —	1.40 to —	1	99	2.53 to 24.5	2.01 to 33
5	95	3.08 to 31.5	1.42 to 46	5	95	3.23 to 17.7	2.00 to 28.5
11.7	88.3	— to 24.5	— to 46	15	85	3.30 to 13.4	1.99 to 21.0
15	85	3.15 to —	1.45 to —	25	75	3.10 to 11.2	1.98 to 16.1
18	82	— to 24	— to 46.5	50	50	2.58 to 8.0	1.95 to 10.55
19.5	80.5	— to 25	— to 46.5	75	25	2.16 to 6.90	1.03 to 7.85
		and					
		36 to 40					
20.3	79.7	— to —	— to 46.5	100	0	1.90 to 6.25	—
		and					
		— to 41					
22	78	— to —	— to 46.5				
		and					
		29 to 31					
25	75	2.95 to 48	1.49 to 46.5				
50	50	2.50 to 51	1.59 to 47				
75	25	2.10 to 50	1.71 to 47.5				
100	0	1.84 to 48	—				

TABLE VI.

Showing the limits for the propagation of flame downwards in mixtures of acetone, benzene, and acetaldehyde with carbon disulphide and air. Temperature  $17 \pm 3^\circ$ .

All calculations are based on the formula on p. 2562.

% Acetone in combustible used.				% Benzene in combustible used.				% Acet. aldehyde in combustible used.			
Lower limit.		Upper limit.		Lower limit.		Upper limit.		Lower limit.		Upper limit.	
Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	2.01	—	34	—	0	2.01	—	0	2.01	—	—
3.8	2.50	2.03	—	—	1.7	2.32	2.00	2	2.56	2.03	—
8.5	3.18	2.07	18.5	27.7	4.2	2.65	1.98	10	3.15	2.12	—
14.9	3.44	2.12	—	—	11.9	3.00	1.93	22.5	3.65	2.28	—
25.0	3.58	2.19	12.6	19.3	20.7	2.87	1.87	50	4.22	2.75	—
50	3.46	2.40	9.7	13.5	35	2.49	1.78	75	4.34	3.37	—
75	3.22	2.66	8.60	10.35	53	2.10	1.68	100	4.36	—	—
100	2.99	—	8.40	—	74	1.78	1.59				
					100	1.48	—				

for propagation flame temperatures appears to hold; that is, to enable propagation of flame to take place, over a good part of the

range the flame temperature attained must be that of the compound containing no sulphur.

TABLE VII.

Showing the relative calorific values of certain lower-limit mixtures of carbon disulphide with benzene, ethyl ether, acetone, and acetaldehyde in air.

Percentage of carbon disulphide vapour present in lower-limit mixture.	Calorific value when mixture contains :				
	Benzene (propn. down).	Ether		Acetone (propn. down).	Acetaldehyde (propn. down).
		(propn. down).	(propn. up).		
0	1114 (1.48)	1148 (1.90)	1111 (1.84)	1205 (2.99)	1134 (4.36)
25	1111 (1.76)	1122 (2.16)	1090 (2.10)	1187 (3.22)	1134 (4.34)
50	1094 (2.15)	1121 (2.58)	1086 (2.50)	1156 (3.46)	1108 (4.22)
75	1064 (2.75)	1084 (3.10)	1032 (2.95)	1072 (3.58)	986 (3.74)

The net calorific values used for the above table were : Benzene 753, ether 604, acetone 403, acetaldehyde 260, carbon disulphide 265.

The figures in brackets specify the total amounts of the mixed vapours containing carbon disulphide in the stated proportions which are necessary to give a lower-limit mixture.

There are, however, three facts which scarcely appear to support the flame temperature theory.

(1) The curves in Fig. 3 show no tendency to follow the dotted line drawn through all vapour mixtures containing 2.01 per cent. of carbon disulphide : that is, the mixtures containing enough of this compound to form a limit mixture when mixed with air alone.

(2) The addition of a small quantity of any one of the other vapours examined to carbon disulphide necessitates the addition of a relatively large amount of the vapour mixture before a mixture with air will propagate flame. Thus the lower limit for downward propagation is raised from 2.01 per cent. to 2.53 by the addition of 1 per cent. of ether to carbon disulphide.

(3) The fall in the calorific value of the limit mixture as the proportion of the sulphur compound in the vapour used increases is far more pronounced the lower the calorific value of the vapour mixed with carbon disulphide—a circumstance not easily explained on the flame temperature theory.

(2) shows that any one of the four vapours used has a powerful inhibitory effect on the propagation of flame in carbon disulphide-air mixtures. In the example given, the addition of 0.025 per cent. of ether necessitates the use of 25 per cent. more carbon disulphide, if the mixture is to propagate flame. The most probable explana-

tion would appear to be that the normal propagation of flame in carbon disulphide-air mixtures is a catalysed action.

The natural idea on coming to this conclusion is that what we may perhaps term the fundamental limit for carbon disulphide in air may agree with the calorific value rule, shown earlier to hold for the other vapours examined. For downward propagation the calculated lower limit for carbon disulphide would be about 4.3 per cent. An examination of Table VIII shows that it appears to be 4.0 per cent.

TABLE VIII.

Showing how the experimental values for the lower limit for the propagation of flame in vapour-carbon disulphide-air agree with those calculated from Le Chatelier's rule, taking the limit for downward propagation to be 4.0 per cent., that for upward to be 3.8 per cent. in carbon disulphide-air.

Percent- age of CS <sub>2</sub> vapour present in lower- limit mixture.	Lower limit when remainder of vapour is:									
	Benzene.		Ether.		Ether.		Acetone.		Acetaldehyde.	
	Downward propagation.		Downward propagation.		Upward propagation.		Downward propagation.		Downward propagation.	
	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.
0	1.48	—	1.90	—	1.84	—	2.99	—	4.36	—
25	1.76	1.76	2.16	2.19	2.10	2.11	3.22	3.19	4.34	4.26
50	2.15	2.16	2.58	2.58	2.50	2.48	3.46	3.42	4.22	4.17
75	2.75	2.81	3.10	3.13	2.95	3.00	3.58	3.69	3.74	4.08
100	2.01	—	2.01	—	1.40	—	2.01	—	2.01	—

The agreement of the calculated and experimental values is generally surprisingly good. The agreement is naturally poor when the proportion of the disulphide in the mixture becomes very high. This is noticeable much earlier with acetaldehyde than with the others.

The upper-limit results shown in Fig. 4 confirm the conclusions drawn from the lower-limit figures, but the inhibitory effect does not appear to reach its maximum value so soon, and therefore calculated results are far less regular. The fundamental value for the upper limit for propagation downwards in carbon disulphide would appear to be in the neighbourhood of 12 per cent.

The theory that the normal combustion of carbon disulphide is catalysed appears to cover satisfactorily the facts available, and it is difficult to see how any other would meet the case so well. The phenomenon is presumably due to the sulphur, and in this connexion it is interesting to recall the behaviour of phosphorus, more particularly as studied by Rayleigh (*Proc. Roy. Soc.*, 1821, [A], 99, 372). He showed that a periodic luminosity exhibited by phosphorus under certain conditions was inhibited

by several oils, certain other organic substances, ammonia, and water. The amount of water required to give this effect appeared to be relatively large. Rayleigh suggested that the propagation of a luminous pulse through a phosphorus-air mixture was due to the provision of nuclei facilitating the action by the combustion of phosphorus. He supposed the inhibiting substances to act by taking prior possession of the nuclei, thus making them unavailable for assisting propagation. Bigelow (*Z. physikal. Chem.*, 1898, 26, 493) found that certain organic substances, such as alcohols, phenols, and benzaldehyde, had a similar inhibitory effect on the oxidation of sodium sulphite by atmospheric air.

The propagation of flame in carbon disulphide-air is presumably catalysed by some product of the combustion, and this effect is inhibited by the presence of any appreciable quantity of any of the combustible vapours tried. When carbon tetrachloride was used, however, it was found that no appreciable change took place in the value of the lower limit of carbon disulphide. Thus in air the limit was 2.01 per cent., in air containing 0.04 per cent. of tetrachloride it was 2.01 per cent., and in air containing 0.10 per cent. of tetrachloride it was 2.00 per cent. Similar results were obtained with carbon dioxide, so that under certain conditions ether would appear to be a better fire extinguisher than either of these two compounds. Certain combustible gases tried seemed to have relatively little effect on the limit of carbon disulphide, and, as has been mentioned in a former communication, fair differences in the amount of water vapour present did not affect the limit appreciably.

The explanation of propagation in carbon disulphide-air now advanced throws some little light on other facts. Thus in a former communication (*loc. cit.*) special note was made of the abnormal behaviour of this compound at both limits when a comparison was made of the limits for upward and downward propagation. It is now seen that the disulphide cool flame could scarcely be expected to behave like that of ether or acetaldehyde, and it is relatively much easier to understand how the great difference between upward and downward propagation occurs at the lower limit. The magnitude of this difference is not easily accounted for on purely thermal grounds, and it appears at least possible that the propagation of flame in hydrogen-air mixtures is also catalysed in some way. The lower limit for upward propagation in this case is less than half that for downward, and there is a further difficulty inasmuch as the calorific value of the lower-limit mixture for upward propagation appears to be insufficient to raise the mixture to its ignition temperature.

The inhibitory effect of certain vapours on the combustion of

carbon disulphide might conceivably provide a test for the detection of small amounts of these in air.

*Summary.*

Limits for the propagation of flame have been determined in various mixtures of two combustible vapours and air. For all the vapours used except carbon disulphide, the mixture results for the lower limit for all directions of propagation and for downward propagation at the upper limit agreed very well with those calculated from the formula proposed by Le Chatelier. Good agreement was obtained throughout in the case of benzene-toluene mixtures, but those containing acetone appeared to be affected by the anomalous behaviour previously observed when examining this compound alone.

In no case did Le Chatelier's rule hold for any direction in which one of the two vapours under examination could propagate a cool flame. When the second vapour gave no cool flame under these conditions, the propagation of a cool flame in the mixture appeared to be hindered by the presence of the second vapour. Some vapours were more effective than others in thus hampering cool flame propagation. By the addition of a vapour giving no cool flame to ether-air, it was found possible to divide the mixture-air propagation range into two, a cool and a normal range, even for upward propagation.

Mixtures containing carbon disulphide gave results differing considerably from those calculated from Le Chatelier's formula. For mixtures which did not contain too much carbon disulphide, the calorific value of the amount of vapour required to give a lower-limit mixture was always much the same. For reasons given, however, it was decided that ordinary propagation in carbon disulphide-air was probably catalysed, presumably by some product of the combustion, but that this catalytic process was inhibited by such vapours as benzene, ether, acetone, and acetaldehyde, although apparently unaffected by small quantities of carbon dioxide and carbon tetrachloride, and little affected by certain combustible gases. The uncatalysed limits for downward propagation in carbon disulphide-air would appear to be about 4.0 per cent. and 12 per cent., values agreeing fairly well with the calorific value rule put forward in Part I. The catalytic character assumed for the combustion process appears to go some length towards explaining the relative values found for the upward and downward limits for propagation in the case of this compound.

Further work is now in progress on the phenomena observed when examining carbon disulphide.

I wish to thank Messrs. Nobel Industries Ltd., and particularly Mr. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

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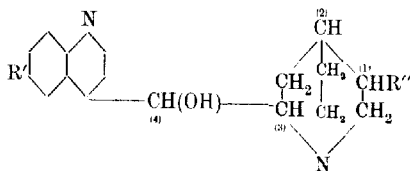
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### CCCVIII.—*The Resolution of Tropic Acid and the Stereochemical Configuration of the Cinchona Alkaloids.*

By HAROLD KING and ALBERT DONALD PALMER.

In the developments of modern chemotherapy, the cinchona group of alkaloids occupies one of the most important positions. This is due to their availability in quantity, to the ease with which their structure can be modified in manifold directions, to the pronounced antimalarial and bactericidal actions of certain members of the group, and the recently discovered value of some in the condition of auricular fibrillation. Owing to the number of workers in this field, resulting in the ever-increasing production of a great number of derivatives of these alkaloids, an understanding of the exact stereochemical interrelation of the main members of the cinchona alkaloids is essential.

The chief alkaloids are embraced by the formula



where  $R' = H, R'' = \cdot CH \cdot CH_2$  in cinchonine and cinchonidine.

$R' = H, R'' = \cdot CH_2 \cdot CH_3$  in hydrocinchonine and hydrocinchonidine.

$R' = OMe, R'' = \cdot CH \cdot CH_2$  in quinine and quinidine.

$R' = OMe, R'' = \cdot CH_2 \cdot CH_3$  in hydroquinine and hydroquinidine.

$R' = OEt, R'' = \cdot CH_2 \cdot CH_3$  in ethylhydrocupreine and ethylhydrocupreidine.

In the van't Hoff sense, they each contain four asymmetric carbon atoms, numbered (1) to (4). These are the foci where the spatial interchange of groups or radicals is reflected in a change in



the magnitude of the specific rotatory power. Thanks to the work of Rabe (*Annalen*, 1910, **373**, 89; *Ber.*, 1922, **55**, [B], 528) it is known that the spatial distribution of the groups around carbon atoms (1) and (2) is the same in all the above-named alkaloids and is dextrorotatory in total effect, and that the spatial distribution about carbon atom (3) is different in each of the pairs named, being dextrorotatory in cinchonine, quinidine, and their hydro-derivatives and in ethylhydrocupreidine, but laevorotatory in cinchonidine, quinine, and their hydro-derivatives and in ethylhydrocupreine. The spatial distribution of groups around carbon atom (4), whether dextro or laevo in effect, was unknown, but is elucidated in this communication. Consequently, although *d*-cinchonine and *d*-hydrocinchonine, for instance, differed from *d*-quinidine and *d*-hydroquinidine, respectively, by a methoxyl group, it was doubtful whether stereochemically a demethoxylated quinidine would be cinchonine or an unknown stereoisomericide.

As one of the present authors (T., 1919, **117**, 476) had shown that when tropic acid is resolved by *l*-quinine, the most sparingly soluble salt is *l*-quinine *d*-tropate, but when resolved by *d*-quinidine, the most sparingly soluble salt is *d*-quinidine *l*-tropate, it was thought that in a closely allied group of alkaloids, like the cinchona group, the stereochemical factor might be of determining influence on the solubility of the various combinations with *d*- and *l*-tropic acid, so that from the experimental results one might be able to say with some degree of certainty that cinchonine, hydrocinchonine, quinidine, and hydroquinidine were stereochemically related, as were cinchonidine, hydrocinchonidine, quinine, and hydroquinine. The experimental results obtained, while of great interest, fail to throw any light on the stereochemical factor, but show the great sensitiveness of solubility to other influences. The results are tabulated below.

Alkaloid.	R'.	R''.	Least soluble tropate.
<i>d</i> -Cinchonine	H	-CH:CH <sub>2</sub>	laevo.
<i>l</i> -Cinchonidine			dextro.
<i>d</i> -Hydrocinchonine			laevo.
<i>l</i> -Hydrocinchonidine			dextro.
<i>l</i> -Quinine	OMe	-CH:CH <sub>2</sub>	laevo.
<i>d</i> -Quinidine			dextro.
<i>l</i> -Hydroquinine			racemic.
<i>d</i> -Hydroquinidine			laevo.
<i>l</i> -Ethylhydrocupreine	OEt	-CH <sub>2</sub> :CH <sub>2</sub>	dextro.
<i>d</i> -Ethylhydrocupreidine			laevo.
<i>d</i> -Cinchotoxine *	H	-CH:CH <sub>2</sub>	laevo.
<i>d</i> -Quinotoxine *	OMe	-CH:CH <sub>2</sub>	laevo.

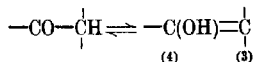
\* In cinchotoxine and quinotoxine, the asymmetric carbon atoms (3) and (4), -CH(OH)-CH, lose their asymmetry, becoming -CO-CH<sub>2</sub>- with simultaneous formation of secondary nitrogen.

It is at once seen that mere reduction of the vinyl group is of influence, at least apparently, for although the dihydro-derivatives of quinine and cinchonidine resolve tropic acid in the same direction as the parent alkaloids, hydroquinidine, unlike quinidine, is unable to resolve the acid, the partial racemate being the most sparingly soluble salt. Again, whilst the levorotatory alkaloids, cinchonidine and hydrocinchonidine, give the *l*-tropate as the least soluble salt, the derivatives, quinine and hydroquinine, differing from the former two by a methoxyl group, bring out the dextro-component. The replacement of the methoxyl group in hydroquinine by the ethoxyl group, as in ethylhydrocupreine, is sufficient, again, to change the direction of resolution. The reverse change in the direction of resolution is observed in the substitution of ethylhydrocupreidine for quinidine, the sole constitutional changes being addition of hydrogen and replacement of methoxyl by ethoxyl. In the case, however, of cinchotoxine and quinotoxine, where, again, the sole difference is substitution of methoxyl for hydrogen, both resolve tropic acid in the same direction. Pasteur (*Compt. rend.*, 1853, 37, 166), on the contrary, found that cinchotoxine and quinotoxine resolved *r*-tartaric acid in different directions. In connexion with this curious effect of the replacement of hydrogen by methoxyl or ethoxyl, it is of interest to recall that when methoxy- or propyloxy-succinic acid is resolved by strychnine, the *lævo*-acid forms the most sparingly soluble salt (Purdie and Bolam, T., 1895, 67, 945), but with the intermediate ethoxysuccinic acid the dextro-acid separates first (Purdie and Williamson, *ibid.*, 961). There are also numerous instances in the literature where the pair *l*-cinchonidine, *l*-quinine, differing by a methoxyl group, resolve acids in different directions.

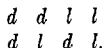
As to the practical value of these alkaloids for resolving tropic acid, the isolation of *d*-tropic acid is best effected by quinine, hydroquinine and ethylhydrocupreidine being almost as good but not quite so accessible, whilst for the isolation of *l*-tropic acid, quinidine and ethylhydrocupreine (optochin) are equally good. With hydrocinchonine, resolution is slow and necessitates the use of alcohol-ether mixtures, whilst with cinchonidine and hydrocinchonidine resolution is very slow owing to formation of mixed crystals.

Some time after the experimental portion of this work was completed, the Vereinigte Chininfabriken Zimmer & Co. described a process (D.R.-P. 330813) for the production of the four possible stereoisomeric alcohols by the reduction of hydrocinchoninone. The rotations of these bases give a clue to the part played by the asymmetric carbon atom (4) in hydrocinchonine and hydrocin-

chonidine. Hydrocinchoninone is the ketone produced by oxidation of hydrocinchonine or hydrocinchonidine and may be represented by the tautomeric grouping



the asymmetry of carbon atoms (3) and (4) being virtually lost. Reduction leads to the production of the four possible alcohols in unequal proportions owing to the effect of the asymmetric atoms (1) and (2). The optical contributions of (3) and (4) in the alcohols may therefore be represented by



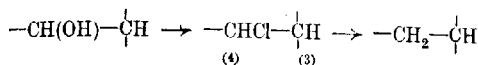
The rotations of the four alcohols are  $+190^\circ$ ,  $+88.5^\circ$ ,  $+48^\circ$ , and  $-98^\circ$ , of which alcohols the first and the last are hydrocinchonine and hydrocinchonidine, respectively, the remaining two being new. As the spatial distribution of groups around carbon atoms (1) and (2) is the same in all four alcohols and is weakly positive in total optical effect, it is evident\* that in the most dextrorotatory, hydrocinchonine with  $[\alpha]_D +190^\circ$ , the carbon atoms (3) and (4) contribute each a dextro-effect, and in the most levorotatory, hydrocinchonidine with  $[\alpha]_D -98^\circ$ , each contributes a laevo effect. This receives support so far as carbon atom (3) is concerned, because Rabe has already shown that (3) is dextrorotatory in quinidine and cinchonine and levorotatory in quinine and cinchonidine. The same applies to the hydroalkaloids.

The optical contribution of (3) and (4) in the alkaloids with  $[\alpha]_D +88.5^\circ$  and  $+48^\circ$  can, of course, be determined experimentally by Rabe's method, namely, by an examination of and identification of their deoxy-bases. The optical contribution of the asymmetric carbon atoms in four of the cinchona alkaloids may therefore be represented with a very considerable degree of certainty in the following abbreviated form.

Alkaloid.	Asymmetric carbon atoms.		
	(1) and (2).	(3).	(4).
Cinchonine	}	+	+
Hydrocinchonine			
Cinchonidine			
Hydrocinchonidine			

\* The principle of optical superposition is assumed here, at least in a semiquantitative sense. It seems justified by the quantitative results, both as regards magnitude and sign of rotation, obtained in the sugar group by Hudson, Levene, and others, and by the singular freedom from optical anomalies in the cinchona alkaloids when submitted to a variety of constitutional changes.

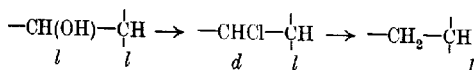
The same argument cannot as yet be applied to quinine and quinidine and their hydro-derivatives, because only two of the four possible alcohols produced by the reduction of hydroquininone are known, namely, hydroquinine and hydroquinidine. It is possible, however, to proceed by analogy and to compare the rotations of the cinchona alkaloids, their monochloro-derivatives, and the deoxy-bases produced by reduction of the latter.



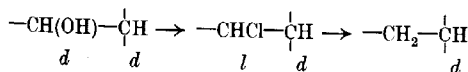
The results are collected in the following table.

	$[\alpha]_D$		$[\alpha]_D$		$[\alpha]_D$
Quinine .....	-158°	Quininechloride .....	+60°	Deoxyquinine .....	-100°
Hydroquinine .....	-142	Hydroquininechloride ...	+43	Deoxyhydroquinine ...	-94
Cinchonidine .....	-111	Cinchonidinechloride ...	+78	Deoxycinchonidine ...	-30
Hydrocinchonidine ...	-98	—	—	—	—
Ethylhydrocupreine...	-144	Ethylhydrocupreinechloride .....	+38	Deoxyethylhydrocupreine .....	-88
Quinidine .....	+243	Quinidinechloride .....	+35	Deoxyquinidine .....	+211
Hydroquinidine .....	+230	Hydroquinidinechloride .....	+20	Deoxyhydroquinidine .....	+187
Cinchonine .....	+224	Cinchoninechloride .....	+56	Deoxycinchonine .....	+179
Hydrocinchonine .....	+190	—	—	Deoxyhydrocinchonine .....	+138

An examination of these rotations shows that there is a very close parallelism between the lævo-alkaloids, their chloro-derivatives, and their deoxy-bases. The same also applies to the dextro-alkaloids. Moreover, the changes in the sign and magnitude of rotation receive their simplest interpretation in terms of the optical signs already deduced from independent evidence, in the case of the alkaloids without methoxyl groups, for asymmetric carbon atoms (3) and (4), namely, both lævo in the lævo-alkaloids and both dextro in the dextro-alkaloids. Thus for the lævo-alkaloids, the carbon atoms concerned may be written



and for the dextro-alkaloids



The simplest explanation is that phosphorus pentachloride causes a change of sign of the contribution of carbon atom (4) in every case, whether a Walden inversion has taken place or not being immaterial, provided the same happens in each case and other atoms are uninfluenced, as indeed is, tacitly assumed in Rabe's deductions of the asymmetric effect of carbon atom (3). On account of this very close analogy, it seems justifiable to incorporate

the methoxy-alkaloids in a similar scheme to the one deduced for the alkaloids without a methoxyl group.

Alkaloid.	Asymmetric carbon atoms.		
	(1) and (2).	(3).	(4).
Quinine	+	—	—
Hydroquinine			
Quinidine	+	+	+
Hydroquinidine			

### EXPERIMENTAL.

#### Resolution of Tropic Acid.

*With Hydroquinine.*—*dl*-Tropic acid (8.3 grams) was neutralised to litmus with hydroquinine (17.6 grams), dissolved in 95 per cent. alcohol. On keeping, 11.5 grams of hydroquinine *d*-tropate separated almost pure, melting at 179–181° and having  $[\alpha]_D -82^\circ$  in absolute alcohol. After recrystallising four times from 95 per cent. alcohol, 6.3 grams of the pure salt were obtained of constant melting point and rotation. By working once more through the mother-liquors, a further 2.2 grams were obtained pure and 2.1 grams melting at 180–181°. The two first crops represent a yield of 66 per cent. of the dextro-component present.

*Hydroquinine d-tropate* crystallises from 95 per cent. alcohol in clusters of glistening, prismatic needles, which are anhydrous. It melts at 184–185° (Found: C = 70.3; H = 7.1.  $C_{20}H_{26}O_2N_2C_9H_{10}O_3$  requires C = 70.7; H = 7.4 per cent.). The specific rotation was determined in absolute alcohol:  $c = 1.012$ ;  $l = 2$  dem.;  $\alpha_D -1.68^\circ$ ;  $[\alpha]_D -83.3^\circ$ .

One gram of hydroquinine *d*-tropate, decomposed by 10 c.c. of 3*N*-hydrochloric acid and extracted with ether, gave without further purification *d*-tropic acid melting at 127–128° and having  $[\alpha]_D +79.5^\circ$  in water ( $c = 0.59$ ). Pure *d*-tropic acid has  $[\alpha]_D +81.6^\circ$ .

*With Hydroquinidine.*—There is no resolution of tropic acid by hydroquinidine, the partial racemic salt being the least soluble.

*Hydroquinidine dl-tropate monohydrate* crystallises from 95 per cent. alcohol in clusters of well-formed prisms, containing  $1H_2O$ . It melts, when air-dried, at 116–118° and when dried at 100°, at 137–139° (Found: in air-dried salt,  $H_2O = 3.9, 3.5$ ; C = 68.0; H = 7.4.  $C_{20}H_{26}O_2N_2C_9H_{10}O_3 \cdot H_2O$  requires  $H_2O = 3.5$ ; C = 68.2; H = 7.6 per cent.). The specific rotation of the hydrate was determined in absolute alcohol:  $c = 1.006$ ;  $l = 2$  dem.;  $\alpha_D +2.77^\circ$ ;  $[\alpha]_D +137.4^\circ$ , whence for anhydrous salt  $[\alpha]_D +142.4^\circ$ .

On several occasions *hydroquinidine dl-tropate* was obtained as the anhydrous salt, crystallising from alcoholic solutions in long, glistening, silky needles. These melted at 137–139°, the melting

point of the dehydrated monohydrate, and passed readily either on standing in the air or on contact with the solution into the hydrated form.

The tropic acid isolated from hydroquinidine *dl*-tropate was inactive and melted at 116—117°.

*With Ethylhydrocupreine.*—From *dl*-tropic acid (8.5 grams) and ethylhydrocupreine (17.5 grams) in alcoholic solution, ethylhydrocupreine *l*-tropate (8.7 grams) was isolated pure. The yield was 60 per cent.

*Ethylhydrocupreine l-tropate* crystallises anhydrous from 95 per cent. alcohol in clusters of small needles. It melts at 199—200° (Found: C = 70.9; H = 7.5.  $C_{21}H_{28}O_2N_2 \cdot C_9H_{10}O_3$  requires C = 71.1; H = 7.6 per cent.). The specific rotation was determined in absolute alcohol:  $c = 1.002$ ;  $l = 2$  dm.;  $\alpha_D = 2.18^\circ$ ;  $[\alpha]_D = 109.3^\circ$ .

From this salt *l*-tropic acid was isolated and without further purification melted at 126—128° and had  $[\alpha]_D = 75.6^\circ$  in water.

*With Ethylhydrocupreidine.*—From *dl*-tropic acid (4.9 grams) and ethylhydrocupreidine (10 grams), ethylhydrocupreidine *d*-tropate (4.6 grams) was isolated pure, and further quantities of slightly less pure salt were obtained from the alcoholic mother-liquors.

*Ethylhydrocupreidine d-tropate* crystallises anhydrous from alcohol in soft, white, voluminous masses of fine needles. It is sparingly soluble in cold alcohol and melts at 182—183° (Found: C = 70.8; H = 7.6.  $C_{21}H_{28}O_2N_2 \cdot C_9H_{10}O_3$  requires C = 71.1; H = 7.6 per cent.). The specific rotation was determined in absolute alcohol:

$$c = 1.011; l = 2 \text{ dm.}; \alpha_D = +3.05^\circ; [\alpha]_D = +150.8^\circ.$$

$$c = 1.012; l = 2 \text{ dm.}; \alpha_D = +3.05^\circ; [\alpha]_D = +150.7^\circ.$$

The tropic acid isolated from this salt melted at 128—130° and gave  $[\alpha]_D = 78.1^\circ$  in water ( $c = 0.61$ ).

From the alcoholic mother-liquors of this salt, the corresponding ethylhydrocupreidine *l*-tropate was isolated in small quantity.

*Ethylhydrocupreidine l-tropate monohydrate* crystallises from alcohol, in which it is readily soluble, in clusters of well-formed prisms. Air-dried, it melts at 121—123° with effervescence at 127°, and when dried at 100° it melts at 131—133° (Found: in air-dried salt,  $H_2O = 3.4$ .  $C_{21}H_{28}O_2N_2 \cdot C_9H_{10}O_3 \cdot H_2O$  requires  $H_2O = 3.6$  per cent.).

Its specific rotation was determined in absolute alcohol:

$$c = 1.029; l = 2 \text{ dm.}; \alpha_D = +2.45^\circ; [\alpha]_D = +118.8^\circ;$$

$$c = 0.856; l = 2 \text{ dm.}; \alpha_D = +2.04^\circ; [\alpha]_D = +119.2^\circ,$$

whence, for the anhydrous salt,  $[\alpha]_D = 123.2^\circ$ . From this salt, ethylhydrocupreidine was recovered, melting at 196° and having

$[\alpha]_D + 225^\circ$  in absolute alcohol ( $c = 0.46$ ) and *l*-tropic acid isolated, melting at  $127\text{--}129^\circ$  and having  $[\alpha]_D - 78^\circ$  ( $c = 0.29$ ).

*With Quinotoxine.*—*dl*-Tropic acid (11.5 grams) and quinotoxine base (21.7 grams) in alcoholic solution gave a crystalline salt which after four crystallisations showed little signs of resolution. After a few crystallisations from water quinotoxine *l*-tropate was readily isolated pure in 58 per cent. yield.

*Quinotoxine l-tropate monohydrate* crystallises best from water, in small, cream-coloured needles. Air-dried, it melts at  $112\text{--}113^\circ$  with effervescence at about  $130^\circ$ , and when dried at  $100^\circ$  it melts at  $116\text{--}118^\circ$  without effervescence (Found: in air-dried salt,  $H_2O = 4.2$ ;  $C = 68.6$ ;  $H = 7.0$ .  $C_{20}H_{24}O_2N_2 \cdot C_9H_{10}O_3 \cdot H_2O$  requires  $H_2O = 3.5$ ;  $C = 68.5$ ;  $H = 7.1$  per cent.). The specific rotation was determined in absolute alcohol:  $c = 0.997$ ;  $l = 2$  dm.;  $[\alpha]_D + 0.17^\circ$ ;  $[\alpha]_D + 8.4^\circ$ , whence for anhydrous salt  $[\alpha]_D + 8.71^\circ$ .

The crude tropic acid isolated from 1 gram of pure quinotoxine *l*-tropate melted at  $126\text{--}128^\circ$  and gave  $[\alpha]_D - 72^\circ$  in water ( $c = 0.46$ ).

*With Cinchotoxine.*—Seventeen grams of cinchotoxine base were neutralised with 9.7 grams of *dl*-tropic acid and the salt from the syrupy solution was recrystallised several times, initially from a mixture of absolute alcohol and dry ether, and finally from 95 per cent. alcohol. The yield of cinchotoxine *l*-tropate was 60 per cent.

*Cinchotoxine l-tropate* crystallises from 95 per cent. alcohol in clusters of fine, matted needles. It melts at  $145\text{--}146^\circ$ . It has a cream colour when pure and forms an almost colourless solution in absolute alcohol, but readily becomes yellowish-brown in colour on boiling. As observed with quinotoxine salts, there is a tendency to resinify (Found:  $C = 72.8$ ;  $H = 7.0$ .  $C_{19}H_{22}ON_2 \cdot C_9H_{10}O_3$  requires  $C = 73.0$ ;  $H = 7.0$  per cent.). The specific rotation was determined in absolute alcohol:  $c = 0.996$ ;  $l = 2$  dm.;  $\alpha_D + 0.205^\circ$ ;  $[\alpha]_D + 10.3^\circ$ .

The tropic acid isolated from 1 gram of this salt was *l*-tropic acid,  $[\alpha]_D - 76^\circ$ , m. p.  $127^\circ$ .

*With Cinchonine.*—All attempts to crystallise any salt from cinchonine and *dl*-tropic acid were fruitless.

*With Hydrocinchonine.*—Molecular quantities of tropic acid (8.3 grams) and hydrocinchonine (14.8 grams) were crystallised together from a mixture of absolute alcohol and ether until the rotation of the product was constant. The yield of hydrocinchonine *d*-tropate was 2 grams.

*Hydrocinchonine d-tropate monohydrate* crystallises in large, hemispherical tufts of needles and also in isolated needles. It melts, when air-dried, from  $178^\circ$  to  $195^\circ$ , effervescing at the latter

temperature and having shown signs of sintering at about  $110^{\circ}$  (Found: in air-dried salt,  $\text{H}_2\text{O} = 4.3$ ;  $\text{C} = 70.0$ ;  $\text{H} = 7.7$ .  $\text{C}_{19}\text{H}_{24}\text{ON}_2 \cdot \text{C}_9\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 3.7$ ;  $\text{C} = 70.0$ ;  $\text{H} = 7.5$  per cent.). The specific rotation was determined in absolute alcohol:

$$c = 0.937; l = 2 \text{ dm.}; \alpha_D + 2.19^{\circ}; [\alpha]_D + 116.7^{\circ};$$

$$c = 0.953; l = 2 \text{ dm.}; \alpha_D + 2.22^{\circ}; [\alpha]_D + 116.8^{\circ},$$

whence, for anhydrous salt,  $[\alpha]_D + 121.3^{\circ}$ . The tropic acid isolated from this salt melted at  $126\text{--}128^{\circ}$  and gave  $[\alpha]_D + 74.4^{\circ}$  in water.

*With Cinchonidine.*—Owing to the formation of a complete series of mixed crystals resolution with this alkaloid is very slow. By crystallising cinchonidine (28.5 grams) and tropic acid (16.0 grams) from alcohol, after five crystallisations, 4 grams of cinchonidine tropate were obtained melting at  $129\text{--}132^{\circ}$  and having  $[\alpha]_D - 73.9^{\circ}$  in absolute alcohol ( $c = 1$ ). In this salt, the tropic acid isolated from 1 gram of material had  $[\alpha]_D - 13.9^{\circ}$ . A second preparation from the mother-liquors, after five crystallisations, weighed 8 grams, had  $[\alpha]_D - 74.7^{\circ}$ , and gave a tropic acid with  $[\alpha]_D - 14.0^{\circ}$ . By combining these crops of partly resolved salt and crystallising three times more, a salt with  $[\alpha]_D - 78^{\circ}$  and weighing only 3 grams was obtained. This gave a tropic acid having  $[\alpha]_D - 24.6^{\circ}$ . As there was no doubt as to the direction in which the resolution was proceeding, cinchonidine *l*-tropate was prepared from the pure components.

*Cinchonidine l-tropate monohydrate* crystallises from alcohol in fine needles. Air-dried, it melts at  $131\text{--}133^{\circ}$ , with slight effervescence (Found: in air-dried salt,  $\text{H}_2\text{O} = 3.2$ ;  $\text{C} = 70.7$ ;  $\text{H} = 7.2$ .  $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{C}_9\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 3.8$ ;  $\text{C} = 70.3$ ;  $\text{H} = 7.2$  per cent.). The specific rotation of the anhydrous substance was determined in absolute alcohol:  $c = 1.108$ ;  $l = 2 \text{ dm.}; \alpha_D - 1.87^{\circ}$ ;  $[\alpha]_D - 84.3^{\circ}$ .

*With Hydrocinchonidine.*—After four crystallisations of equimolecular quantities of *dl*-tropic acid (8.3 grams) and hydrocinchonidine (14.8 grams) from a mixture of absolute alcohol and ether, a crude hydrocinchonidine tropate was obtained with  $[\alpha]_D - 55.8^{\circ}$  in absolute alcohol. This salt gave a tropic acid having  $[\alpha]_D - 11.4^{\circ}$  in water. From the combined mother-liquors, after four more crystallisations, a hydrocinchonidine tropate, which gave a tropic acid having  $[\alpha]_D - 20.7^{\circ}$ , was obtained. The resolution was thus in the direction of hydrocinchonidine *l*-tropate.

*Hydrocinchonidine l-tropate monohydrate* was prepared from molecular quantities of the pure components and recrystallised



twice from a mixture of absolute alcohol and ether. It crystallises in hemispherical tufts of glistening needles. Air-dried, it softens at about  $80^{\circ}$  and effervesces at about  $110^{\circ}$ , and when dried at  $100^{\circ}$  it melts at about  $130^{\circ}$  (Found: in air-dried salt,  $\text{H}_2\text{O} = 4.0$ ;  $\text{C} = 69.9$ ;  $\text{H} = 7.5$ .  $\text{C}_{19}\text{H}_{24}\text{ON}_2 \cdot \text{C}_9\text{H}_{10}\text{O}_3 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 3.7$ ;  $\text{C} = 70.0$ ;  $\text{H} = 7.5$  per cent.). The specific rotation was determined in absolute alcohol:  $c = 1.05$ ;  $l = 2$  dm.;  $\alpha_D - 1.33^{\circ}$ ;  $[\alpha]_D - 63.2^{\circ}$ , whence, for anhydrous salt,  $[\alpha]_D - 65.7^{\circ}$ .

The authors are greatly indebted to Messrs. Boots Pure Drug Co. and to Messrs. Howards & Sons for a free supply of *r*-tropic acid and the cinchona alkaloids, respectively, used in this investigation.

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### CCCIX.—*The Solubility and Volatility of the Nitrobenzaldehydes.*

By NEVIL VINCENT SIDGWICK and WILFRED MARSDEN DASH.

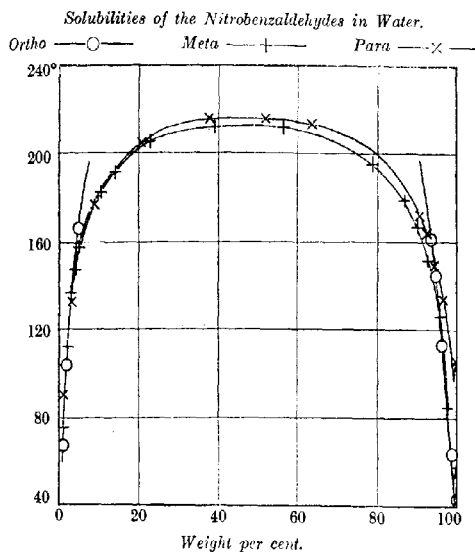
BOTH the nitro-group and the aldehyde group are often found in the most markedly abnormal benzene derivatives, such as the nitrophenols, the nitrobenzoic acids, and the hydroxy-aldehydes and aldehyde-acids. We have therefore examined the nitrobenzaldehydes, in which the two groups occur together.

*Preparation of Materials.*—*o*-Nitrobenzaldehyde. The commercial product was recrystallised twice from alcohol and twice from ligroin. The melting points given in the literature are  $43.5$ – $44.5^{\circ}$  (Gabriel and Meyer, *Ber.*, 1881, **14**, 829);  $45$ – $46^{\circ}$  (Vanino, "Organische Präparate," 1914, p. 484);  $46^{\circ}$  (Friedländer and Henriques, *Ber.*, 1881, **14**, 2803). We did not find it possible to raise the melting point above  $43.5^{\circ}$  (corr.); to make certain that the material was dry, a portion was heated at  $80^{\circ}$  for half an hour, but its melting point was unchanged. In working with this substance it is necessary to use a subdued light, in order to avoid conversion into nitrosobenzoic acid. *m*-Nitrobenzaldehyde was made by the nitration of benzaldehyde at  $5^{\circ}$  by a solution of potassium nitrate in concentrated sulphuric acid (Friedländer and Henriques, *loc. cit.*; Ehrlich, *Ber.*, 1882, **15**, 2010). It melted at  $58.0^{\circ}$  (corr.) after recrystallisation from aqueous alcohol and drying at  $105^{\circ}$ . The paracompound used was Kahlbaum's purest material, twice recrystallised from aqueous alcohol, washed with sodium carbonate (to

remove any acid) and water, and dried at  $110^{\circ}$ . It melted at  $106.5^{\circ}$  (corr.).

*Determination of Solubilities.*—These were measured in sealed bulbs, or at lower temperatures in a Beckmann apparatus. The temperatures of the triple points (solid aldehyde and two liquids) in presence of water were determined in a series of separate experiments, and the composition obtained by extrapolation on the two-liquid curve. The complete solubility curves were realised in water for the meta- and para-compounds, with critical solution tempera-

FIG. 1.



tures of  $212^{\circ}$  and  $216^{\circ}$ , but the ortho-curves could not be taken above  $160^{\circ}$ , as decomposition then set in. The benzene used was free from thiophen, and melted at  $5.32^{\circ}$ .

The results are given in the following tables, and plotted on Figs. 1 and 2. In Table I, the points at which solid aldehyde is present are marked *s*. In Table II, those points at which solid benzene separates are marked *b*; at the other points, the second phase is solid aldehyde.

*Volatility in Steam.*—This was determined for each of the three isomerides in the apparatus already\*described (T., 1920, 417, 396). The composition of the distillate was estimated by the method of

TABLE I.  
Solubility of the Nitrobenzaldehydes in Water.

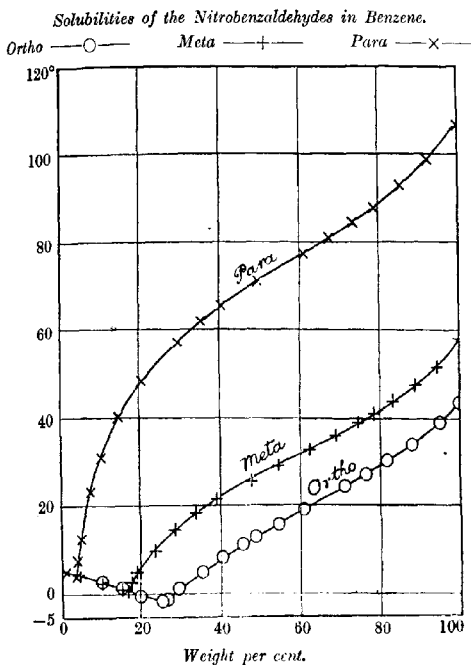
Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
0.70	66.9°	0.39	40.5°	0.97	90.2°
1.53	103.1	0.96	75.1	2.91	132.4
4.75	166.0	1.95	111.9	8.78	176.5
—	—	3.01	136.4	20.67	205.4
93.56	161.7	3.95	147.1	37.77	215.5
94.80	145.1	4.92	157.3	51.92	215.7
96.49	113.5	10.51	181.0	63.19	213.4
99.00	63.8	14.03	191.4	90.65	172.6
100	43.5	23.35	205.4	92.74	164.6
		39.62	211.8	96.70	134.2
		56.23	211.7	100	106.5
		78.77	195.3		
		86.75	170.3		
		90.18	167.0		
		92.87	152.0		
		95.67	126.2		
		97.83	85.2		
		100	58.0		
Triple point :					
99.9	39.7°	99.6	51.0°	98.2	97.1°
Critical solution temperature :					
	—		212°		216°

TABLE II.  
Solubility of the Nitrobenzaldehydes in Benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
0.00	5.3° <i>b</i>	0.00	5.3° <i>b</i>	0.00	5.3° <i>b</i>
1.17	5.1° <i>b</i>	1.20	5.0° <i>b</i>	1.00	5.0° <i>b</i>
2.47	4.7° <i>b</i>	2.40	4.7° <i>b</i>	2.00	4.6° <i>b</i>
3.51	4.4° <i>b</i>	4.28	4.3° <i>b</i>	2.75	4.4° <i>b</i>
4.98	3.9° <i>b</i>	4.98	4.0° <i>b</i>	3.57	4.1° <i>b</i>
10.12	2.7° <i>b</i>	10.14	2.4° <i>b</i>	4.06	7.5°
15.18	1.2° <i>b</i>	15.15	1.0° <i>b</i>	5.01	12.6°
20.09	-0.4° <i>b</i>	16.16	0.9°	7.57	23.4°
25.23	-1.5° <i>b</i>	17.55	2.8°	10.15	30.8°
26.85	-1.2°	19.03	4.9°	15.00	40.5°
29.59	+1.2°	23.55	9.8°	20.53	49.3°
35.35	4.9°	28.43	14.7°	29.61	47.5°
40.24	8.2°	33.77	18.5°	35.31	62.2°
45.48	11.3°	38.91	21.7°	40.42	65.7°
48.84	13.0°	47.68	25.6°	49.82	71.3°
54.40	15.8°	54.53	29.4°	61.12	77.2°
60.74	19.4°	62.30	33.0°	67.56	81.0°
70.98	24.6°	68.87	36.3°	73.54	84.9°
76.28	27.2°	74.35	39.2°	78.85	87.8°
81.60	30.2°	78.36	41.2°	85.54	93.0°
87.82	34.1°	83.23	43.9°	92.83	98.6°
95.08	39.1°	88.80	47.7°		
100	43.5°	94.49	51.7°		
		100	58.0°		
Eutectic point :					
26.50	-1.7°	15.75	-0.8°	3.80	+41°

trache (*Sitzungsber. K. Akad. Wiss. Wien*, 1891, 100, IIb, 424; 892, 101, IIb, 311), by conversion into the hydrazone with excess of phenylhydrazine, and determination of the excess by oxidation with copper sulphate and measurement of the hydrogen evolved.

FIG. 2.



The results are given in the following table. Each value is the mean of from three to five determinations, which in no case differed by more than 5 per cent. The corrected values are the vapour pressures which the pure liquids would have at 100°, calculated by the method previously described (Sidgwick and Ewbank, T., 1921, 119, 997), it being assumed that the relative lowering of the vapour pressure by the water is the same as at the triple point, where it can be calculated from the heat of fusion.

	Ortho.	Meta.	Para.
Weight per cent. in distillate .....	1.89	1.27	0.85
Vapour pressure in mm. $\times 100$ { obs. ....	1.74	1.16	0.76
corr. ....	1.88	1.32	0.90

*Nominal Heats of Solution in Benzene.*—These were calculated from the solubility curves by means of the usual formula

$$\log_e \frac{s}{s_1} = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right).$$

The results are given in Table III, and plotted on Fig. 3.

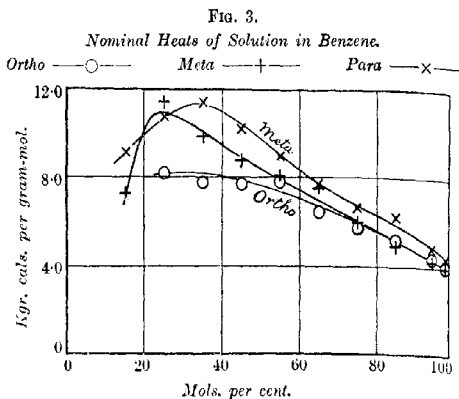


TABLE III.

*Nominal Heats of Solution in Benzene.*

Mean mol. per cent.	Heat of Solution in kgr.-cals.		
	Ortho.	Meta.	Para.
95	4.39	4.26	4.87
85	5.21	4.89	6.32
75	5.75	5.98	6.58
65	6.45	7.55	7.66
55	7.78	8.08	8.97
45	7.72	8.80	10.26
35	7.83	9.92	11.45
25	8.20	11.45	10.78
15	—	7.32	9.15

#### *Discussion of Results.*

The influence of position on the physical properties of the nitrobenzaldehydes is not large, or in other words they are only slightly abnormal. It is unfortunate that the decomposition of the ortho-compound at higher temperatures made it impossible to determine its critical solution temperature. The closeness of the curves for the meta- and para-compounds in water is very marked (their critical solution temperatures are only 4° apart), but this occurs with abnormal compounds (for example, with the nitrophenols) as well as

with normal. The ortho-curves (in water), so far as they go, show a smaller solubility, as we should expect, but not much smaller. The heats of solution in benzene lead to the same result. The following table gives the increase in the heat of solution (maximum value divided by that at 95 molecules per cent.) for the nitrobenzaldehydes as compared with the corresponding figures for the chloroacetanilides \* (almost normal), the nitroanilines (definitely abnormal), and the nitrophenols (highly abnormal):

	Ortho.	$Q_{\text{max}} \div Q_{95}$ Meta.	Para.
$\text{NO}_2\text{CHO}$ .....	1.87	2.88	2.58
$\text{Cl.NHAc}$ .....	1.66	1.93	2.35
$\text{NO}_2\text{NH}_2$ .....	3.63	3.78	4.88
$\text{NO}_2\text{OH}$ .....	1.48	3.39	5.60

The volatilities again show an almost normal behaviour. The boiling points of the ortho- and meta-compounds are only  $8^\circ$  apart ( $156^\circ$  and  $164^\circ$  at 23 mm.: that of the para has not been determined); the vapour pressures at  $100^\circ$  as deduced from the volatilities in steam do not differ widely, as is shown by the following comparison of their relative values (para = 1) with those of the other derivatives:

Relative Vapour Pressures at  $100^\circ$ .

	Ortho.	Meta.	Para.
$\text{NO}_2\text{CHO}$ .....	2.09	1.48	1
$\text{Cl.NH}_2$ .....	2.43	1.08	1
$\text{NO}_2\text{NH}_2$ .....	23.0	5.00	1
$\text{NO}_2\text{OH}$ .....	35.3	2.37	1

We may therefore conclude that the nitrobenzaldehydes are only very slightly abnormal, to about the same extent as the chloroanilines.

A general survey of the results of these investigations, while it confirms the view already expressed that abnormality requires the simultaneous presence of two suitable ("active") substituent groups in the nucleus, also shows that these two groups act in two different ways, like the chromophore and auxochrome groups in a dye: to be abnormal, the isomerides must contain (1) a group making them sensitive, and (2) another group which can act on this sensitiveness. The following table summarises the effects of six of the most active groups examined (0 indicates normality, + distinct abnormality, and ++ great abnormality. Where the

\* The chloroanilines would no doubt give similar values, but their melting points are so low that the heats of solution can only be measured over a narrow range.

symbols are placed in brackets, the compounds have not been fully investigated).

	OH.	NH <sub>2</sub> .	CO <sub>2</sub> H.	CHO.	NO <sub>2</sub> .	Cl.
OH .....	(++)		++	++	++	++
NH <sub>2</sub> .....		(+)	(+)		+	0
CO <sub>2</sub> H .....	++	(+)	(+)	+	+	0
CHO .....	++		+		0	(0)
NO <sub>2</sub> .....	++		+	0	0	(0)
Cl .....	++	0	0	(0)	(0)	(0)

All these groups are capable of activating a sensitive group, but the sensitiveness itself diminishes as we pass along the table downwards or from left to right. The nitro-group causes abnormality in phenol (very large), in benzoic acid (large), and in aniline (fairly large), but not in chlorobenzene or nitrobenzene, and scarcely at all in benzaldehyde. The aldehyde group is similar: it activates hydroxyl and carboxyl, but scarcely the nitro-group, and not chlorine. The chlorine atom is still more restricted in its action; it has so far only been found to produce abnormality in the phenols.

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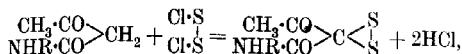
### CCCX.—The Formation and Properties of Dithio- ketones ( $R_2C:S:S$ ) and Dithio-ethers ( $R_2S:S$ ). Part III.

By KUVIRJI GOSAI NAIK and MAHADEO DATTATRAYA AVASARE.

THE experiments described here were undertaken with a view to test the hypothesis advanced by one of us (T., 1921, 119, 1232), namely, that interaction of sulphur monochloride and a compound containing the methylene radicle depends on the nature of the groups attached to the two remaining valencies of the carbon atom. It was shown that either one or both of the hydrogen atoms of the methylene radicle were brought into activity, the course of the reaction depending on the total negativity of the two carbonyl groups with their attached radicles.

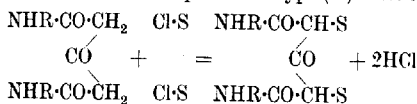
The work so far recorded was carried on with compounds which are derivatives of malonic or acetonedicarboxylic acid. Experiments have now been made with (1) the anilide, (2) the *o*-toluidide, and (3) the *p*-toluidide of acetoacetic acid. Of these compounds, only the first has been described (Knorr, *Annalen*, 1886, 236, 75), whereas (2) and (3) do not seem to have been prepared. When these three compounds were treated with sulphur monochloride

in dry benzene, reaction took place more readily and more vigorously than in the case of the corresponding derivatives of malonic and acetonedicarboxylic acids. Stable disulphides were formed in each case. Thus,

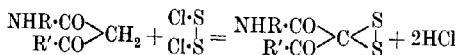


where R is the phenyl or tolyl group. Here the total negativity of the groups attached to the reactive methylene group is greater than in the cases of the corresponding malonic and acetonedicarboxylic acid derivatives.

Considering the three compounds (i)  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHR}$ , (ii)  $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHR}$ , and (iii)  $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHR}$ , it will be seen that the total negativity of the carbonyl groups with their attached radicles in the case of (i) is due to two groups, one of which,  $\text{CO} \cdot \text{NHR}$ , is common to all three compounds, and the other, the acetyl group, is more negative than the partly neutralised group,  $\text{CO} \cdot \text{NHR}$ , which is present in (ii) and (iii). Again, the negative effect of the central carbonyl group in (iii) is divided between the two adjacent methylene groups, so that the total negative effect on each methylene group is smaller than that on a single methylene group, when linked as  $-\text{CO} \cdot \text{CH}_2 \cdot \text{CO}-$ , as in cases (i) and (ii). Hence it is to be expected that the two methylene groups in (iii) will be less reactive than the one in (ii), which in turn will be less reactive than that in (i). Such has actually been found to be the case. Whereas compounds of type (iii) react thus,

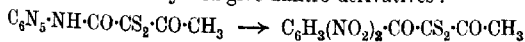


those of types (ii) and (i) behave as follows,



where R' is the methyl or anilino-group. Reaction in the case of (i), however, proceeds very much faster than in the case of (ii), in fact, the reaction proceeds vigorously even in the cold. Such behaviour is in accordance with the theory.

It was stated in Parts I and II (*loc. cit.*, pp. 382, 1233) that it is possible to nitrate the compounds there mentioned without destroying the dithio-grouping, which behaves as a remarkably stable residue. The dithio-compounds now described can also be nitrated in a similar way and give dinitro-derivatives:





This behaviour obviously lends further support to the view previously advanced that the dithio-grouping in these compounds is structurally different from that present in  $\beta\beta'$ -dichlorodiethyl disulphide and similar compounds, and that sulphur monochloride is capable of reacting in the two forms indicated (*loc. cit.*).

Further work is in progress with a view to throw additional light on the problem, by studying the influence of such reagents as sulphur dichloride, sulphuryl chloride, thionyl chloride, etc., on these and corresponding derivatives of cyanoacetic acid.

#### EXPERIMENTAL.

*Dithioacetoacetanilide*.—Two grams of acetoacetanilide and 2.5 grams of sulphur monochloride ( $S_2Cl_2$ ) were heated under reflux with 50 c.c. of dry benzene for two hours. Reaction started in the cold, hydrogen chloride gas being vigorously evolved. When the evolution of the gas ceased, the product was filtered and washed thoroughly with dry benzene to free it from the excess of sulphur monochloride. The solid residue, after repeated purification from a mixture of benzene and petroleum, melted and decomposed at  $125^\circ$  (Found: S = 26.92.  $C_{10}H_9O_2NS_2$  requires S = 26.78 per cent.).

The acetoacetanilide required for the experiment was prepared by Knorr's method (*loc. cit.*). The product obtained was very pure, but the yield was very small. It was crystallised from a mixture of benzene and ligroin.

The *dinitro*-derivative of the above dithioacetoacetanilide was prepared by warming the thio-compound with a sufficiency of nitric acid (*d* 1.5), reaction being very vigorous. The nitration product was precipitated by the addition of a minimum of water, and after being washed with nitric acid and with water was obtained as a brown powder, decomposing at  $167^\circ$  (Found: N = 12.90; S = 18.82.  $C_{10}H_7O_6N_3S_2$  requires N = 12.76; S = 19.45 per cent.).

*Acetoacet-p-toluidide*.—Acetoacetic ester and *p*-toluidine in equimolecular quantities were heated in a sealed tube at  $120$ – $125^\circ$  for five hours. The alcohol having been evaporated, the residue was cooled in a freezing mixture and the resulting crystalline mass washed with a mixture of benzene and ligroin and subsequently crystallised from the same solvent; the substance obtained melted at  $95^\circ$ . It is very soluble in alcohol or benzene and sparingly soluble in ligroin (Found: N = 7.56.  $C_{11}H_{13}O_2N$  requires N = 7.33 per cent.).

*Dithioacetoacet-p-toluidide*.—Equal quantities (3 grams) of the above *p*-toluidide and sulphur monochloride were heated under reflux with 100 c.c. of benzene for three hours. After hydrogen

chloride ceased to be evolved, the product was treated in the same way as the corresponding anilide derivative. It began to decompose at  $120^{\circ}$  and melted at  $140^{\circ}$  (Found: S = 25.28.  $C_{11}H_{11}O_2NS_2$  requires S = 25.29 per cent.).

The dinitro-derivative was prepared in the same way as the corresponding dinitroanilide, and obtained as a yellow powder decomposing at  $170^{\circ}$  (Found: N = 12.16; S = 18.85.  $C_{11}H_9O_4N_2S_2$  requires N = 12.24; S = 18.65 per cent.).

*Acetoacet-o-toluidide*.—This substance was prepared in the same way as the corresponding *p*-tolyl derivative, and after recrystallisation from benzene and petroleum melted at  $107^{\circ}$ . It is very soluble in alcohol or benzene and sparingly soluble in ligroin (Found: N = 7.62.  $C_{11}H_{13}O_2N$  requires N = 7.33 per cent.).

*Dithioacetoacet-o-toluidide*.—The *o*-toluidide was treated with sulphur monochloride in the same way and in the same proportions as the corresponding para-derivative. The product, on repeated purification from a mixture of benzene and petroleum, melted and decomposed at  $167^{\circ}$  (Found: S = 25.26.  $C_{11}H_{11}O_2NS_2$  requires S = 25.29 per cent.).

We take this opportunity to record our thanks to the Chemical Society for a grant which has partly defrayed the expense of this investigation.

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[Received, August 30th, 1922.]

### CCCXI.—The Triazo-group. Part XXII.\* *Cinnamic Acid Chlorohydrin and its Conversion into $\alpha$ -Triazo- $\beta$ -hydroxy- $\beta$ -phenylpropionic Acid.*

By MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE.

THE derivatives of phenylserine which should lead to a synthesis of picrorocellin (this vol., p. 816) appeared likely to be obtainable from  $\alpha$ -triazol- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid,  $C_6H_5CH(OH)CHN_3CO_2H$ , and we find that this compound is readily prepared from the chlorohydrin of cinnamic acid (phenylchlorolactic acid). In accumulating the necessary chlorohydrin, however, we encountered a pronounced divergence from the observations of Read and Andrews (T., 1921, 119, 1774), and the compound having been first described more than fifty years ago (Glaser, *Annalen*, 1868, 149, 80), it seems remarkable that fresh facts may

\* Part XXI was published T., 1912, 101, 1359.

still be learned regarding it. We do not suggest that the results of Read and Andrews are recorded inaccurately, although we followed their prescription as exactly as possible; we prefer to believe that addition of hypochlorous acid to cinnamic acid is an action more than usually sensitive to slight variation of experimental conditions.

Whereas from cinnamic acid (20 grams) Read and Andrews obtained the dichloride (0.4 gram), chlorostyrene (1.5 grams), and the chlorohydrin (23.8 grams), our experiments, repeated many times with uniform results, have never given the dichloride and have produced only a very small proportion of chlorostyrene; the yield of chlorohydrin averaged 21.6 grams, whilst in addition there was invariably isolated a volatile, neutral substance (4.1 grams) melting at  $56^{\circ}$ , having the empirical formula of chlorostyrene chlorohydrin,  $C_8H_8OCl_2$ , and appearing to have escaped the notice of earlier workers. This result arose alike from cinnamic acid of synthetic and vegetable origin; it was not varied by conducting the operation in dim light, although speed of reaction was much greater in direct sunshine, and it was also not affected by using cylinder chlorine instead of the gas produced from hypochlorite. Furthermore, the chlorohydrin was never isolated in a manner so simple as might be inferred from the description given by Read and Andrews, its purification being a matter of some difficulty; in fact, we have found it much more convenient to use the method of Erlenmeyer and Lipp (*Annalen*, 1883, **219**, 185) which, by a simple modification, readily produces the chlorohydrin in good yield and in excellent form, accompanied by chlorostyrene.

The melting point of cinnamic acid chlorohydrin calls for remark. Read and Andrews mention  $78-80^{\circ}$  for the monohydrate, thus agreeing with Glaser and with Erlenmeyer and Lipp, who further state that the anhydrous compound melts at  $104^{\circ}$ . Whilst confirming the latter observation, we have repeatedly noticed that the freshly prepared chlorohydrin, after being drained on porous earthenware, melts indefinitely below  $50^{\circ}$ , and when recrystallised from warm water melts at  $50-52^{\circ}$ , rising to  $56^{\circ}$  after two days in air, remaining constant at that temperature. In this connexion, it is noteworthy that Zimmer and Stieglitz (*Ber.*, 1889, **22**, 3140) record  $56.5^{\circ}$  for the hydrated modification and  $86^{\circ}$  for the anhydrous acid; moreover, Rassow and Burmeister (*J. pr. Chem.*, 1911, [ii], **84**, 473) state that the hydrated acid melts at  $56-57^{\circ}$  and changes into a labile anhydrous acid melting at  $86^{\circ}$ , of which the stable form melts at  $102-103^{\circ}$ . We find that the anhydrous material (m. p.  $104^{\circ}$ ) takes up moisture on exposure to air, and may then begin to melt as low as  $90^{\circ}$ , whilst the hydrated specimens, if left in a

sulphuric acid desiccator during many days, do not begin to melt below  $92^{\circ}$ ; consequently, we believe the true melting points to be  $56^{\circ}$  (hydrated) and  $104^{\circ}$  (anhydrous).

$\alpha$ -Triazo- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid, prepared from the chlorohydrin and sodium azide, is much more stable than the chloro-compound, and when compared with phenyltriazooacetic acid (Forster and Müller, T., 1910, **97**, 138) illustrates the result of separating the phenyl radical from the carbon atom which carries the carboxyl and triazo-groups. Nevertheless, it is decomposed by hot alkalis, giving benzaldehyde, nitrogen, ammonia, and hydrazoic acid; the methyl ether, on the other hand, retains the carbon chain intact although the triazo-group is removed.

#### EXPERIMENTAL.

##### *Preparation of Cinnamic Acid Chlorohydrin.*

*Method of Read and Andrews.*—A large glass jar containing 1600 c.c. of water and 2 c.c. of concentrated sulphuric acid was surrounded with melting ice. During vigorous agitation, a brisk stream of chlorine was passed into the liquid, and a solution of sodium cinnamate, prepared by dissolving 20 grams of cinnamic acid in 67 c.c. of 2*N*-sodium hydroxide solution diluted with 200 c.c. of water, was added in quantities of 20 drops, further addition being delayed until the consequent turbidity had disappeared. In bright daylight, the chlorine was rapidly absorbed, ice being added from time to time during the one and a half to two hours occupied by the operation. The slightly turbid liquid was filtered from a small quantity of suspended solid, extracted twice with light petroleum, then saturated with salt and extracted twice with ether, this being dried with sodium sulphate and distilled, when a viscous, pale amber-coloured oil remained. The product crystallised to a thick, honey-like mass which could not be filtered or drained on earthenware until rubbed with 20 c.c. of water; it was then filtered by the aid of the pump, kneaded with 40 c.c. of saturated brine, and again filtered, the crystalline chlorohydrin melting at about  $52^{\circ}$ . After twenty-four hours, the two filtrates containing oil and brine had yielded a further quantity of crystalline chlorohydrin which melted indefinitely at  $45$ – $50^{\circ}$ , and the oil filtered therefrom was extracted with ether; when dried with sodium sulphate and distilled, the residue remained liquid during many weeks, after which a few crystals appeared. Meanwhile, the petroleum extract was distilled on the water-bath; the residual oil had the odour of chlorostyrene, but became almost completely solid during forty-eight hours, the crude product melting at  $56^{\circ}$ . Finally, the oil

which had been filtered with brine from the chlorohydrin, and which had remained liquid for an indefinite period, was found to be a mixture of chlorohydrin and the foregoing neutral compound removed by the light petroleum; it was therefore treated with aqueous sodium carbonate (10 per cent.) until faintly alkaline, the neutral component remaining undissolved and removable by ether, whilst the chlorohydrin, melting at  $45-50^{\circ}$ , was precipitated by adding dilute sulphuric acid and saturating the liquid with salt, the neutral compound being isolated by subjecting to steam distillation the residue left on distilling the ether.

Six experiments carried out as above did not show any divergence from one another. A total yield of chlorohydrin amounting to 130 grams (73.5 per cent. of the amount calculated for  $C_9H_9O_3Cl \cdot H_2O$ ) was obtained together with 25 grams of the neutral product melting at  $56^{\circ}$ . The small quantity of sticky solid which had been filtered from the reaction-liquor, and having the odour of chlorostyrene, was rubbed with a few c.c. of light petroleum and drained on earthenware; it weighed 1 gram (from 120 grams) and consisted of unchanged cinnamic acid. The dichloride could not be found, and the total amount of chlorostyrene from 120 grams of cinnamic acid could not have exceeded 2 grams. The source of chlorine was a cylinder of compressed gas, but action proceeded in the same manner and led to the same quantitative results when the halogen was prepared from bleaching powder. Cinnamic acid from storax was also used, and did not differ from the synthetic material in behaviour. Protection from sunlight merely retarded the action without altering the character or yield of the products, whilst in dull red light the addition of hypochlorous acid proceeded too slowly for efficient working.

*Modified Method of Erlenmeyer and Lipp.*—Sodium hypochlorite was prepared by saturating with chlorine a well-stirred solution of crystallised sodium carbonate (143 grams) in water (1000 c.c.) at  $4^{\circ}$ . Sodium cinnamate from the acid (75 grams), water (1000 c.c.) and sodium carbonate (54 grams, anhydrous) was agitated at  $4^{\circ}$  during rapid addition of the hypochlorite; after half-an-hour in ice the liquid, which became increasingly turbid, was treated with sulphur dioxide until excess of active chlorine had been reduced, and then acidified with hydrochloric acid (250 grams of  $d\ 1.19$ ), which precipitated a sticky, crystalline paste. This having been separated, the liquid was extracted twice with light petroleum and saturated with salt, precipitating crystals which melted at about  $52^{\circ}$ . The product was extracted with ether, this being dried with sodium sulphate and distilled, leaving a viscous, pale yellow oil which rapidly solidified to a friable cake, quite different in character

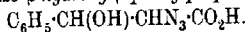
from the honey-like product obtained by the method described above. The oily residue from evaporation of the petroleum extract had an aromatic odour reminiscent of chlorostyrene; having been united with the sticky, crystalline paste obtained on adding hydrochloric acid to the original mixture, it was subjected to steam distillation, which carried over a volatile, limpid oil and left impure cinnamic acid in the flask. The yield of chlorohydrin from 70 grams of cinnamic acid (75 grams less 5 grams recovered) amounted to 74 grams (corresponding with 71·8 per cent. of the quantity calculated for  $C_9H_9O_3Cl \cdot H_2O$ ) together with 18 grams of the volatile oil. Thus, in view of the much larger quantities manipulated at one operation, the superior readiness with which the by-product can be removed, and the more convenient form in which the chlorohydrin emerges, the modified method of Erlenmeyer and Lipp is, in our opinion, preferable to that of Read and Andrews.

*Purification through the Sodium Salt.*—The chlorohydrin (50 grams) was made into a paste with water (100 c.c.) and treated with sodium carbonate (13·25 grams) in water (50 c.c.), dissolution being followed immediately by crystallisation of the sodium salt in flat, lustrous needles. After being filtered and washed with brine, the product (28 grams) was dissolved in water (150 c.c.) and acidified with sulphuric acid (7 grams) diluted with water (10 c.c.), the crystalline acid melting at about 55°. Dissolved in water at about 40° and allowed to cool spontaneously, the acid separated first as an oil; on adding enough cold water to dissolve this, and then stirring vigorously, lustrous, silky needles appeared, and the liquid set to a paste of crystals within half-an-hour, the air-dried product melting at 56° (Found: C = 49·2; H = 5·1; Cl = 16·2.  $C_9H_9O_3Cl \cdot H_2O$  requires C = 49·4; H = 5·0; Cl = 16·2 per cent.). During two days in the desiccator over sulphuric acid the melting point rose to 95°, and the product was then recrystallised by dissolving 2 grams in 25 grams of chloroform and adding 20 grams of light petroleum; the acid separated in rosettes of flat, transparent prisms, and melted at about 84°, giving indications of softening at about 60°, but after two days in the desiccator it melted at 104° with only slight previous softening. In this condition, 1·45 grams required 41 grams of chloroform for complete dissolution, 53 grams of light petroleum being then added; the freshly withdrawn crystals melted at 102° without previous shrinking, but after twelve hours in a vacuum desiccator melted sharply at 104° (Found: C = 53·7; H = 4·9; Cl = 17·7.  $C_9H_9O_3Cl$  requires C = 53·9; H = 4·5; Cl = 17·7 per cent.). When separation from the above mixture takes place slowly, the chlorohydrin crystallises in flat, transparent, six-sided prisms, well formed and separated.

*The Neutral By-products.*

*Solid, obtained by the Method of Read and Andrews.*—The residue from the light petroleum rapidly solidified, and having been drained on earthenware from a small quantity of oil having the odour of chlorostyrene, was recrystallised from warm light petroleum, in which it dissolves readily, separating in massive, transparent, rhomboidal prisms melting at  $56^{\circ}$  (Found: C = 50.3, 50.4; H = 4.2, 4.4; Cl = 37.1, 37.1.  $C_8H_8OCl_2$  requires C = 50.2; H = 4.2; Cl = 37.2 per cent.). The substance is very readily volatile in steam, the vapour being pungent and sternutatory. When heated in aqueous alcohol with ammoniacal silver oxide, separation of silver chloride occurs, whilst benzoic acid and benzaldehyde are produced. Boiling aniline is without action, but cold, concentrated sulphuric acid transforms the compound into a colourless, amorphous material which has not been crystallised, being insoluble in common organic media. The empirical formula is that of a chlorohydrin of chlorostyrene, very probably  $C_8H_7\cdot CH(OH)\cdot CHCl_2$ .

*Liquid, obtained by the Method of Erlenmeyer and Lipp.*—The residue from the light petroleum remained liquid and was therefore distilled in steam. The volatile oil, having been collected by ether and dried with sodium sulphate, was distilled under atmospheric pressure, and the principal fraction, boiling at  $197$ – $200^{\circ}$ , was redistilled almost completely at  $197$ – $199^{\circ}$  (Found: C = 69.3; H = 5.1; Cl = 24.7.  $C_8H_7Cl$  requires C = 69.3; H = 5.0; Cl = 25.6 per cent.). It thus appears to be chlorostyrene, which boils at  $199^{\circ}$ .

 *$\alpha$ -Triazo- $\beta$ -hydroxy- $\beta$ -phenylpropionic Acid,*

Sodium phenylchlorolactate (20 grams), air-dried, was dissolved in cold water (100 c.c.), mixed with sodium azide (9 grams) in water (30 c.c.), and maintained at about  $80^{\circ}$  during one and a half hours, the liquid becoming slightly turbid and developing a faintly aromatic odour. The cold solution was filtered from a very small quantity of crystalline material and acidified with sulphuric acid (50 per cent.), the snow-white, crystalline precipitate, together with further amounts obtained on adding salt and by extraction with ether, weighing 10.7 grams. After recrystallisation from benzene, the triazo-acid melted at  $122^{\circ}$  (Found: C = 52.2; H = 4.4; N = 20.2.  $C_9H_9O_3N_3$  requires C = 52.2; H = 4.3; N = 20.3 per cent.). One gram of the acid requires about 4 c.c. of hot water or 1½ c.c. of hot benzene for dissolution, stellate aggregates of lustrous needles being deposited on cooling. Effervescence with concen-

trated sulphuric acid is very vigorous, but very slow with stannous chloride. When heated with aqueous sodium hydroxide (10 per cent.), the dissolved triazo-compound rapidly yields benzaldehyde along with ammonia, accompanied by slight effervescence; when action is complete, sodium azide is recognisable in the liquid.

*Methylation.*—A mixture of the triazo-acid (2 grams) and methyl sulphate (5 grams) was shaken with 20 per cent. aqueous sodium hydroxide (10 c.c.), added in small quantities. After extraction with ether, addition of sulphuric acid to the aqueous liquid precipitated a colourless oil which became crystalline as the dissolved ether evaporated. The filtered product (1.5 grams) was warmed with light petroleum (17 grams), which deposited striated aggregates of prisms melting at  $91^{\circ}$  (Found: N = 18.7;  $\text{CH}_3\text{O}$  = 13.9.  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$  requires N = 19.0;  $\text{CH}_3\text{O}$  = 14.0 per cent.).  *$\alpha$ -Triazo- $\beta$ -methoxy- $\beta$ -phenylpropionic acid* is freely soluble in cold benzene and dissolves readily in warm water; it is much more stable than the hydroxy-compound towards hot, aqueous sodium hydroxide, which removes the triazo-group very slowly and does not produce benzaldehyde.

The foregoing experiments were conducted in the Davy-Faraday Laboratory of the Royal Institution.

ROYAL INSTITUTION, W.1.

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CCCXII.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part VII. Absorption Spectra of the Halogen Derivatives of some Cyclic Compounds, and their Bearing on the Question of an Oxygen-Halogen Linking.*

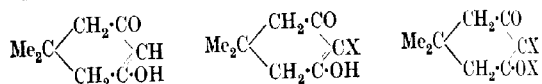
By HUGH GRAHAM and ALEXANDER KILLEN MACBETH.

THE labile nature of the halogen atom in different types of organic compounds has been substantially demonstrated in the previous papers of this series (T., 1921, **119**, 1356; this vol., pp. 892, 904, 1116, 2169, 2527). Hypotheses to account for the reactivity of the halogen atom in some of the compounds examined had been proposed by various workers, a notable suggestion being that the labile nature of the halogen atom is connected with certain structural arrangements, the reactive compounds containing an oxygen-halogen linking (Vorländer and Kohlmann, *Annalen*, 1902, **322**, 239; Willstätter and Hottenroth, *Ber.*, 1904, **37**, 1775). The question



of such a linking occurring in the molecule has already been examined (Graham and Macbeth, this vol., p. 1109), and the evidence obtained from a study of the absorption spectra of bromomalonic derivatives and nitroparaffins indicates that the view is untenable in these cases. It seemed of interest to extend the observations to other types of compounds containing reactive halogen atoms, and the results obtained furnish further support for the view that an oxygen-halogen linking does not occur in the reactive substances.

The compounds now examined include 1:1-dimethylcyclohexane-3:5-dione and *cyclohexanespirocyclohexane-3:5-dione* and their halogen derivatives. Vorländer and his collaborators prepared the dimethyldihydroresorcinol compound and examined its properties and those of its halogen derivatives. The parent dione and its monohalogen derivatives behave as monobasic acids, forming neutral sodium salts. Their alcoholic solutions become deeply coloured on the addition of ferric chloride, and therefore the compounds exist in the enolic form. The dihalogen derivatives differ entirely from the monohalogen compounds in chemical properties, the latter resisting the action of boiling alkali whereas the former are readily decomposed by warm alkali or sodium carbonate solution, one of the halogen atoms being removed. To account for these differences, and the marked oxidising properties of the dihalogen compounds, the following formulæ were proposed:



Vorländer further suggested that the bromoxyl structure probably occurred quite frequently in organic compounds, and advocated an oxygen-halogen linking in the case of dibromobarbituric acid (Baeyer, *Annalen*, 1863, **127**, 229) and the dihalogen derivatives of diketohydrindenes (Zincke, *Ber.*, 1887, **20**, 3216; 1888, **21**, 498, 2390).

The absorption spectra of 1:1-dimethylcyclohexane and its derivatives are expressed in Figs. 1 and 2. Reference to the curves shows that the parent dione has a strong selective absorption, the head of the band occurring at  $1/\lambda$  3550, and persisting to a dilution of  $N/10,000$ . The absorption of the sodium salt is materially the same as that of the parent compound. The monohalogen derivatives also show the strong selective effect noted in the case of the parent dione, the band having much the same persistence as that observed in the previous cases. The band is, however, slightly shifted towards the red. A similar effect has been recorded in the case of pyridine and the chloropyridines (Hartley, *T.*, 1885, **47**, 685; Purvis, *Proc. Camb. Phil. Soc.*, 1908, **41**, 568; Baker and Baly,

T., 1907, 91, 1124). In these cases it is found that the normal effect of attaching chlorine to the ring is to increase the persistency of the band observed, and to shift it towards the red. The shift, however, is greater than that noted in the present cases, and the spatial position of the substituents is connected with the change in the absorption.

FIG. 1.

- 1:1-Dimethylcyclohexane-3:5-dione.  
 ..... 4-Bromo-1:1-dimethylcyclohexane-3:5-dione.  
 - - - - - 4:4-Dichloro-1:1-dimethylcyclohexane-3:5-dione.  
 ..... 4:4-Dibromo-1:1-dimethylcyclohexane-3:5-dione.

FIG. 2.

- 1:1-Dimethylcyclohexane-3:5-dione (in presence of NaOEt).  
 ..... 4-Chloro-1:1-dimethylcyclohexane-3:5-dione.  
 - - - - - 4-Chloro-4-bromo-1:1-dimethylcyclohexane-3:5-dione.  
 - - - - - 4-Chloro-1:1-dimethylcyclohexane-3:5-dione (in presence of NaOEt).

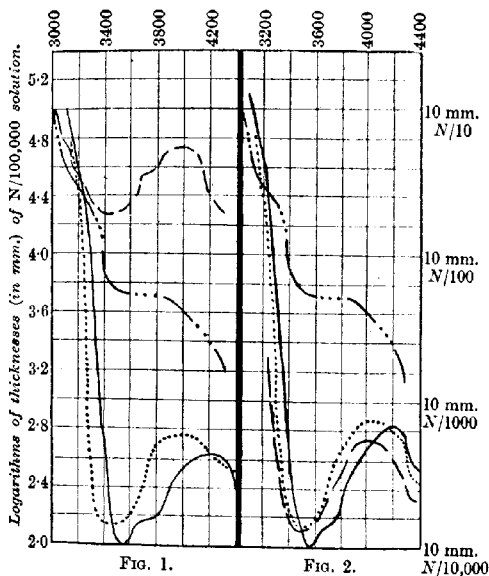


FIG. 1.

FIG. 2.

The absorption spectra of the dihalogen derivatives of 1:1-dimethylcyclohexane-3:5-dione are seen to differ entirely from those of the parent substance, the monohalogen derivatives, and the sodium salts. The strong selective action characteristic of these enolic compounds disappears, and, instead, a shallow band or a region of rapid extension is noted, the persistence of the band extending little

beyond dilutions of  $N/100$ . It is therefore evident that the dihalogen compounds differ structurally from the parent dione and the mono-halogen derivatives, and it seems reasonable to conclude that in them the enolic structure is absent: the bromoxyl structure is, we think, therefore ruled out, and the presence of an oxygen-halogen linking disproved.

Thorpe and his collaborators have for some time been engaged in a study of the *spiro*-compounds, as an outcome of which it is hoped to gain an insight of the nature of valency as it occurs in carbon compounds. Norris and Thorpe (T., 1921, **119**, 1199) prepared *cyclohexanespirocyclohexane-3:5*-dione and its halogen derivatives. These compounds possess the structural features of the dimethyldihydroresorcinol derivatives examined by Vorländer, and show similar chemical properties. The presence of an oxygen-halogen linking in these compounds has been disproved experimentally by these workers by preparing the same chlorobromo-derivative by the alternative methods of chlorinating the monobromo-compound and brominating the monochloro-derivative. Similar proof was adduced in the case of the dimethyldihydroresorcinol derivatives. The examination of the absorption spectra of this series of compounds has afforded further proof of the absence of an oxygen-halogen linking, and the results are expressed in the curves shown in Fig. 3.

It will be seen that the absorption curves of *cyclohexanespirocyclohexane* compounds are practically identical with the graphs of the corresponding 1:1-dimethyl*cyclohexane* derivatives. Becker and Thorpe (T., 1920, **117**, 1579) directed attention to the fact that when the normal angle between two of the valencies of a carbon atom is altered as a result of their inclusion in a ring, the groups attached by means of the remaining valencies apparently take up altered positions in space. This effect in the compounds referred to above does not express itself in the absorption spectra of the substances, and this is not unexpected in view of the fact that Drude (*Ann. Physik*, 1904, [iv], **14**, 677, 936) showed that the mobile particles which cause absorption in the visible and ultra-violet regions are valency electrons: absorption in the ultra-violet and visible portions of the spectrum is therefore a highly constitutive property, and it is not surprising that the factor referred to above is not of sufficient magnitude to manifest itself in the spectra of the compounds. The additional weighting of the molecule in passing from the dimethyldihydroresorcinol to the *spiro*-compound is also insufficient to cause any difference in the absorptive power of the substance. The similarity between the spectra of the parent diones and their salts, and of the monohalogen compounds and their sodium compounds, is in agreement with the results recorded by Wright (T., 1914, **105**,

669) on the relation between the absorptive powers of acids and their salts (compare also Hantzsch and Scharf, *Ber.*, 1913, **46**, 454, 3570; Henri, *Ber.*, 1913, **46**, 464, 3650).

FIG. 3.

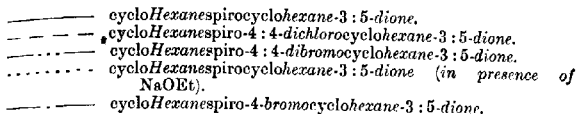


FIG. 4.

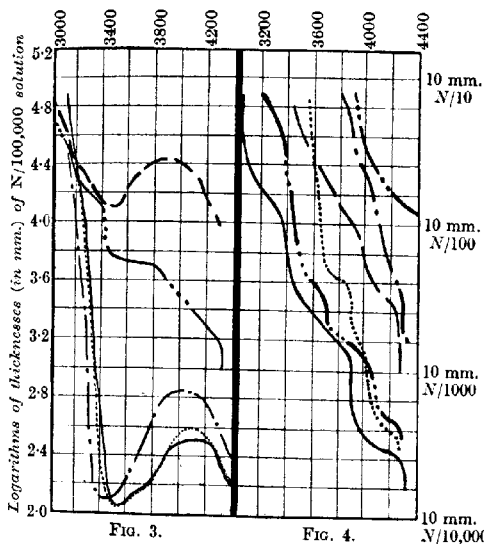
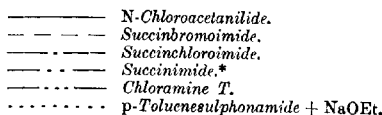


FIG. 3.

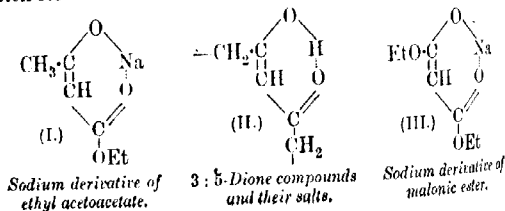
FIG. 4.

\* The curve for succinimide is taken from Ley and Fischer, *Ber.*, 1913, **46**, 327.

Some reference may be made to a point of secondary interest which has arisen in the course of the work. It is well known that ethyl acetoacetate and its *O*-ethers show no result of selective action in their absorption spectra, but the metallic derivatives are characterised by a deep band (Baly and Desch, *T.*, 1904, **85**, 1029; 1905, **87**, 766). On the other hand, the enolic forms of 1:1-dimethyl-

cyclohexane- and cyclohexanespirocyclohexane-3 : 5-diones and their monohalogen derivatives are characterised by a strong selective absorption which is almost identical with the absorptions of their respective sodium salts. Hantzsch (*Ber.*, 1910, **43**, 3049) made an extended study of the absorption spectra of ethyl acetoacetate and its derivatives and concluded that the deep band developed in the presence of alkali represented the absorption of the sodium derivative. To differentiate between the structure of this compound and the enolic form of the ester itself he proposed a "ring" formula (I) for the sodium derivative, and suggested that an internal salt was formed by the calling into play of an auxiliary valency of the metallic atom. If it is to be assumed that sodium has an auxiliary valency, it would seem illogical to refuse one to the hydrogen atom: and Hantzsch's assumption in itself does not account for the difference between the spectra of the enolic form of ethyl acetoacetate and the sodium derivative. It has been pointed out (Brannigan, Macbeth, and Stewart, T., 1913, **103**, 406) that a distinction between the forms may be drawn if consideration is given to the conception of valency proposed by Gebhard (*J. pr. Chem.*, 1911, [ii], **84**, 561). According to this view, since there is very slight ionisation in the enolic form of ethyl acetoacetate, we are entitled to assume that the union between the hydrogen and oxygen atoms of the hydroxyl group is a strong one and there is no development of an "ionised" valency: in the case of the sodium salt, which is much more readily dissociated, it is assumed that the union is weaker and the auxiliary or "ionised" valency required by Hantzsch's formula is developed.

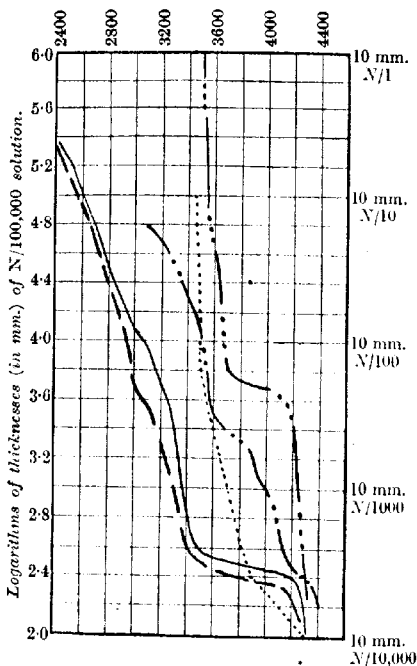
The diones referred to are known to exist in the enolic form and behave as monobasic acids, forming neutral sodium salts. The hydrogen atom of the hydroxyl group is therefore capable of pronounced ionisation, and so may develop an "ionised" valency in the same way as the sodium atom: no difference is therefore to be expected in the spectra of the parent compound and its sodium salt. It is interesting to note that the substances now discussed fall into line with those hitherto examined in which a strong selective action is noted, for the same type of six-membered "ring" may be written for each.



The absorption spectra of some nitrogen haloids and the corresponding parent compounds are expressed in the curves shown in Figs. 4 and 5. The spectra of the sulphonamides and their metallic derivatives are much the same, as is seen on reference to the cases

FIG. 5.

————— 2-Nitrotoluene-*p*-sulphonamide.  
 - - - - - " " + NaOEt.  
 . . . . . Dichloramine T.  
 ———— *p*-Toluenesulphonamide.  
 ..... Acetanilide.\*



\* The spectrum of acetanilide is taken from Crymble, Stewart, Wright, and Glendinning, T., 1911, **99**, 451.

of *p*-toluenesulphonamide and 2-nitrotoluene-*p*-sulphonamide. The halogen derivatives show absorption of much the same type as that of the compounds from which they are derived, an increase in the general absorption being noted in all the cases examined. This effect is illustrated in the spectra of acetanilide and *N*-chloroacetanilide; succinimide, succinylchlorimide, and succinylbromimide;

*p*-toluenesulphonamide, chloramine T, and dichloramine T. The introduction of the halogen atom into these substances appears to produce no radical change in the constitution of the compounds and therefore the reactivity is not to be explained on such grounds.

The absorption spectra of all the types examined furnish direct evidence against the presence of an oxygen-halogen linking in the reactive halogen compounds, and the view that the labile nature of the halogen atom in such substances is accounted for by such a structure appears to be untenable.

We wish to express our thanks to Professor A. W. Stewart and the Queen's University of Belfast for access to their spectroscope, and to Mr. R. W. Kinkead, M.Sc., for assistance in the photographic work.

CHEMICAL RESEARCH LABORATORY,  
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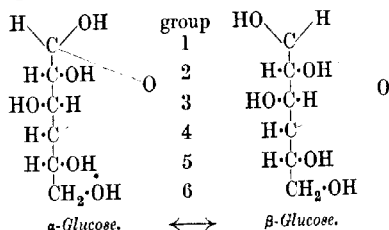
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[Received, September 25th, 1922.]

### CCCXIII.—Optical Rotations of the Sugars. Part I. *The Aldohexoses and Aldopentoses.*

By JOHN GWILLIAM MALTBY.

THE difference in the molecular rotations of the  $\alpha$ - and  $\beta$ -forms of the aldoses is approximately constant (Hudson, *J. Amer. Chem. Soc.*, 1909, 31, 66), so that on van't Hoff's theory of optical superposition group 1 has a fixed rotational value.

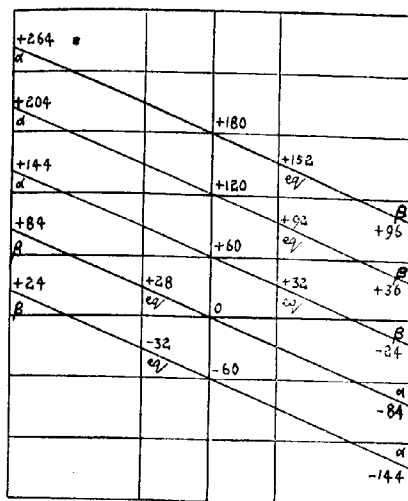


The rotation due to the combined effects of the other groups will be the mean of the rotations of the  $\alpha$ - and  $\beta$ -forms, which will be called the  $(\alpha + \beta)/2$  value. It will be shown that the difference between the  $(\alpha + \beta)/2$  values for epimeric aldopentoses and aldohexoses, which differ only with regard to group 2, is constant. A method of classifying the sugars in two groups (*d* and *l*) is given,

depending on the sign of the  $(\alpha + \beta)/2$  value. Also, by solving equations derived from the configurations and rotations, the rotational value of each asymmetric group is calculated.

As the ratio of the  $\alpha$ - and  $\beta$ -forms in the equilibrium mixture is 1:2, and the difference between their rotations is constant (Hudson,

FIG. 1.



$$\frac{\alpha + \beta}{2}$$

<i>d</i> -Hexoses.			<i>l</i> -Pentoses.		
Name.	Configuration.	$\frac{\alpha + \beta}{2}$ value.	Name.	Configuration.	
Galactose .....	5 4 3 2	180	Arabinose .....	4 3 2	
Talose .....	- + + -	60	Ribose .....	+ + +	
Glucose .....	- + + -	120			
Mannose .....	- - + +	0			
Gulose .....	- + - -	60	Lyxose .....	+ - -	
Idose .....	- + - +	-60	Xylose .....	+ - +	

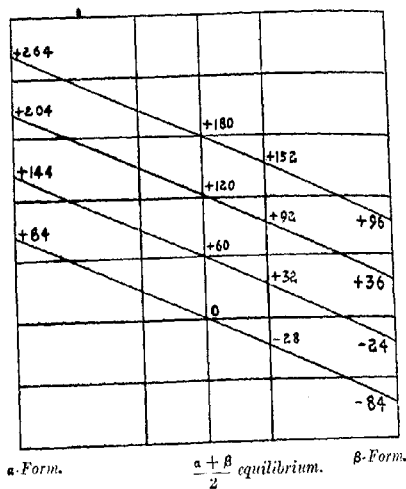
*loc. cit.*), the latter can be calculated from the rotation of the equilibrium mixture, which is the only value known in the case of some sugars. If these values are plotted graphically as in Fig. 1, using Rosanoff's classification (*J. Amer. Chem. Soc.*, 1906, 28, 114), it will be seen that the difference between the  $(\alpha + \beta)/2$  values for epimeric sugars is constant, and that there is a similarity between pentoses and hexoses of similar configuration. The rotations can be found in papers by van Eckenstein and Blanksma (*Chem.*



*Weekblad*, 1908, 5, 777; 1909, 6, 373; 1913, 10, 664) and Hudson and Yanovsky (*J. Amer. Chem. Soc.*, 1917, 39, 1013).

It will be noticed, however, that in the case of mannose, idose, and xylose, the  $\alpha$ -form has been placed vertically under the  $\beta$ -forms of the other sugars. In these three cases the  $(\alpha + \beta)/2$  value is zero or negative, whilst in all the other cases it is positive. This gives a new method, dependent on the rotation, for classifying the

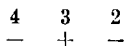
FIG. 2.



Hexoses.		$\alpha + \beta$	Pentoses.	
Name.	Configuration. 5 4 3 2	value.	Name.	Configuration. 4 3 2
Galactose .....	- + + -	180	Arabinose .....	+ + -
Glucose .....	- - + -	120		
Talose .....	- + + +	60	{ Ribose .....	+ + +
Idose .....	+ - + -		{ Xylose .....	- + -
Gulose .....	- + - -		{ Lyxose .....	+ - -
Mannose .....	+ + - -	0		

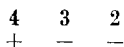
sugars, as opposed to that of Fischer (*Ber.*, 1894, 27, 3208) based on the chemical relations of the sugars to *d*-glucose, and that of Rosanoff (*J. Amer. Chem. Soc.*, 1906, 28, 114) based on whether the sugar could be synthesised by the cyanohydrin synthesis from *d*-glycer-aldehyde. If the rotations of the sugars in which the  $(\alpha + \beta)/2$  value is positive are plotted as in Fig. 2, all the  $\alpha$ , equilibrium, and  $\beta$  values occur on the same vertical lines.

If the configurations of the above sugars are compared, it will be seen that all those in which group 4 is negative have the configuration



These are abnormal, as they will not form hydrazones with diphenylmethanedimethyldihydrazine (Votoček, *Ber.*, 1917, 50, 35; *Z. Zuckerind. Bohm.*, 1919, 43, 574; von Braun, *Ber.*, 1917, 50, 42).

Similarly, all those in which group 3 is negative have the configuration



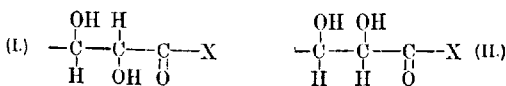
These sugars include lyxose and mannose, which are abnormal as regards their  $\alpha$ - and  $\beta$ -rotations (Hudson and Yanovsky, *loc. cit.*), and these are the only two cases where there is a large discrepancy between the values used in the graphs above and the experimental values.

It will also be noticed that mannose is the only sugar given above which has a negative value for the equilibrium mixture. Now mannose is abnormal as regards its activity to permanganate in alkaline and in neutral solution (Armstrong and Hilditch, *T.*, 1920, 117, 1088), and the fact that no  $\beta$ -derivatives have yet been prepared pure, and only one mannoheptose can be obtained by the cyanohydrin synthesis.

On equating the rotations and configurations given on the graphs above, and solving in the manner applied to derivatives of the sugar acids (Levene and Meyer, *J. Biol. Chem.*, 1915, 23, 145; 1916, 26, 355; 1917, 31, 623; Hudson, *J. Amer. Chem. Soc.*, 1917, 39, 462; Hudson and Komatsu, *ibid.*, 1919, 41, 1141), the molecular rotational value of each asymmetric group is found to be as follows:—

Group.....	5	4	3	2	1
Pentoses .....		+60°	+60°	-60°	±84°
Hexoses .....	-30°	+30°	+60°	-60°	±84°

Using these values, it can be shown that allose and altrose should have the same rotations as mannose and glucose, respectively. The fact that the rotations due to groups 2 and 3 are equal and opposite explains Anderson's observations (*J. Amer. Chem. Soc.*, 1911, 33, 1510) that monosaccharoses containing the grouping I



(X = H or CH<sub>2</sub>·OH) are strongly dextrorotatory, and reversed positions of H and OH give strong laevorotation, whilst the grouping II gives only weak rotations.

Hudson and Yanovsky (*loc. cit.*) calculated the molecular rotational value for group 2 as  $-45^{\circ}$ .

Anderson (*J. Physical Chem.*, 1916, 20, 269) has put forward the hypothesis that  $\alpha$ -glucose has a butylene-oxide, and  $\beta$ -glucose a propylene-oxide, structure, and has also found a relation to exist between the configuration and the rotation of the sugars.

In conclusion, the author wishes to thank Prof. F. S. Kipping, F.R.S., for his interest, and the Department of Scientific and Industrial Research for a grant which enabled the work to be carried out.

CHEMISTRY DEPARTMENT,

UNIVERSITY COLLEGE, NOTTINGHAM. [Received, August 15th, 1922.]

#### CCCXIV.—*The System Ammonium Sulphate-Glucinum Sulphate-Water at 25°.*

By HUBERT THOMAS STANLEY BRITTON.

In a previous paper (Britton and Allmand, T., 1921, 119, 1464), it was stated that the method of preparing glucinum sulphate by dissolving the hydroxide, precipitated by ammonium hydroxide, in sulphuric acid proved unsuccessful, as the precipitate retained sufficient ammonia to produce the double sulphate of glucinum and ammonium. After the precipitate had been dried on the water-bath for several days, it still retained ammonia but in amount insufficient to yield the double sulphate. The crystallisation of glucinum sulphate thus depends on the character of the three-component system glucinum sulphate-ammonium sulphate-water.

Attempts to obtain crystals of glucinum sulphate from alcoholic solutions, by pouring hot concentrated solutions of these precipitates in sulphuric acid into alcohol, failed. If solutions containing ammonium sulphate were poured into alcohol, the mixed liquids formed two distinct layers, the lower one being somewhat viscous. From these alcohol-sulphuric acid solutions of the precipitates solid phases separated only when the solution of the precipitate which had been added was exceptionally concentrated. These solid phases were deliquescent and contained varying amounts of

the two sulphates in proportions which corresponded with no definite double salt. It will be observed from the data of the ternary system—ammonium sulphate–water–ethyl alcohol—enumerated on pages 65 and 66 of Seidell's "Solubilities," that the upper layer is always largely alcoholic and has a small ammonium sulphate content, whereas the lower layer is mainly aqueous and consequently has a large capacity to dissolve ammonium sulphate. The solubility of glucinum sulphate in alcohol is very small, but increases with the proportion of water introduced. Thus, if glucinum sulphate were included in the system just referred to, much would dissolve in the lower layer and little in the upper. In effect, the lower layer would be made up of ammonium and glucinum sulphates, water, and alcohol in small quantity.

This small amount of alcohol would have, in all probability, no other effect than to lower slightly the solubilities of the two sulphates. To a great extent, therefore, crystallisation from the lower layer will depend on the system ammonium sulphate–glucinum sulphate–water. Moreover, the use of alcohol in the crystallisation of glucinum sulphate is deleterious when the solutions contain ammonium sulphate.

The object of this work was therefore (1) to ascertain to what extent ammonia is retained by glucinum hydroxide, and (2) to investigate the ternary system ammonium sulphate–glucinum sulphate–water at a suitable temperature, namely, 25°.

## EXPERIMENTAL.

### I. *Investigation of Glucinum Hydroxide Precipitates.*

The gelatinous glucinum hydroxide was precipitated in the cold from sulphuric acid and aqueous solutions of the sulphate, and rapidly filtered through a Büchner funnel, so that as much adhering mother-liquor as possible was removed. The products were dried either at room temperature or on a water-bath for varying periods. When dry, they were amorphous and no ammonia could be detected by smell. On examination, however, they were found to contain much ammonia, the amount of which was estimated. Further, it was found that the precipitates also held sulphate the molar proportion of which was slightly greater than that of the ammonia held by the respective precipitates. Hence the ammonia had been retained in the form of ammonium sulphate, and the slight excess of sulphate corresponded with the glucinum sulphate which had been carried down by the hydroxide precipitate. The following two sets of data, given in molar proportions, are typical analyses of the products obtained :

	GIO.	H <sub>2</sub> O.	GlSO <sub>4</sub> .	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	Remarks.
1.	1.00	1.111	0.043	0.614	From H <sub>2</sub> SO <sub>4</sub> solution. Dried for fifty hours at 100°.
2.	1.00	3.112	0.039	0.444	From H <sub>2</sub> O solution. Dried for ten days at 15°.

Much of the ammonium sulphate could doubtless have been extracted by repeated decantation. That the first sample would contain the larger amount of ammonium sulphate was to be expected, as a large quantity was formed in the mother-liquor before precipitation commenced. In the other case, the ammonium sulphate, of which, it appears, a relatively large amount was adsorbed, was produced by double decomposition. Again, in the former case, it will be observed that the effect of heating for a time at 100° was to drive off much of the water, which therefore appears to be mechanically held, the water retained being a little more than that required by the formula  $\text{Gl}(\text{OH})_2$  (compare van Bemmelen, *J. pr. Chem.*, 1882, [ii], 26, 227). Attempts were made to isolate such a substance from the gelatinous precipitate. It was found that if the dried glucinum hydroxide precipitate were finely ground and boiled with a large quantity of water, the adsorbed ammonium sulphate could be easily and completely extracted, together with a little of the glucinum sulphate. The following is a typical analysis of a precipitate, so treated, and dried for a day on a water-bath :

1 mol. GIO : 1.17 mols. H<sub>2</sub>O : 0.019 mol. GlSO<sub>4</sub>.

After drying at room temperature for six weeks, the water content fell to 1.11 mols. It was exceedingly difficult to wash out the last traces of glucinum sulphate. Attempts to obtain glucinum hydroxide, agreeing exactly with the formula, by continued heating at 100° were unsuccessful.

## II. Isotherm at 25° of the System Ammonium Sulphate-Glucinum Sulphate-Water.

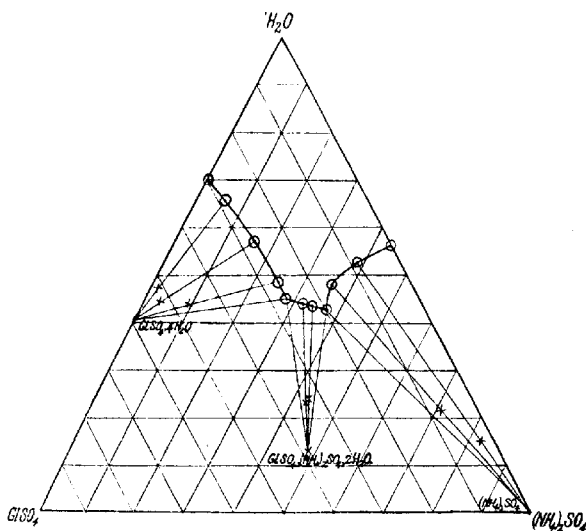
The method adopted was that already described (*loc. cit.*). The eutectic points were obtained by making solutions of glucinum sulphate and ammonium sulphate, in proportions which could be ascertained approximately from the phase diagram, and stirring them with the appropriate solid phases until equilibrium was attained. The glucina and sulphate were estimated by standard methods. The amounts of ammonia calculated from these data were checked by the distillation method.

The table gives the composition of the various liquid phases and their respective "rests" in grams per 100 grams.

Liquid phases.			" Rests."			Solid phases.
$\text{GISO}_4$ .	$(\text{NH}_4)_2\text{SO}_4$ .	$\text{H}_2\text{O}$ .	$\text{GISO}_4$ .	$(\text{NH}_4)_2\text{SO}_4$ .	$\text{H}_2\text{O}$ .	
29.94	0	70.06	59.35	0	40.65	$\text{GISO}_4 \cdot 4\text{H}_2\text{O}$ .
28.56	5.77	65.67	51.16	1.37	47.47	"
27.26	15.66	57.08	52.18	3.07	44.75	"
26.68	24.99	48.33	46.90	9.12	43.98	"
26.79	28.09	45.12	—	—	—	$\text{GISO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{GISO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .
24.04	32.20	43.76	33.64	42.84	23.52	$\text{GISO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .
22.08	34.26	43.66	32.83	42.93	24.24	"
19.72	37.56	42.72	—	—	—	$\text{GISO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ .
16.04	35.88	48.08	7.59	71.09	21.32	$(\text{NH}_4)_2\text{SO}_4$ .
8.62	38.60	52.78	2.82	82.29	14.89	"
0	43.45	56.55	—	—	—	"

As these solubilities are comparatively large, the isotherm can be represented conveniently on the ordinary triangular scale.

FIG. 1.



It will be noticed that the field of the double salt is quite small and that the point of intersection of its tie-lines indicates the constitution of the double salt as being  $\text{GISO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

By referring to the composition of the dried glucinum hydroxide precipitates given in the table, it will be seen that supersaturated solutions of these precipitates in sulphuric acid, on attaining equilibrium at room temperature, will deposit crystals of glucinum

sulphate tetrahydrate, and if the degree of supersaturation is sufficiently high both the tetrahydrate and the double sulphate will separate. It is evident that the solid phases deposited from the alcoholic solutions must have been glucinum sulphate tetrahydrate and the double salt due to the exceptionally high concentrations of the solutions which had to be employed. In conclusion, it is advisable that the greater part of the ammonia should be removed from the glucinum hydroxide precipitate before proceeding with the preparation of glucinum sulphate; otherwise the double salt and glucinum sulphate tetrahydrate together, or the double salt alone, may separate, as was found to be the case in several instances.

The author wishes to record his thanks to the Chemical Society for a grant from its Research Fund.

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[Received, October 2nd, 1922.]

CCCXV.—*Orientation of the 1:4- and 1:5-Dimethylglyoxalines. Mode of Fission of 5-Aminoglyoxalines.*

By FRANK LEE PYMAN.

SOME years ago, it was shown (T., 1910, **97**, 1814) that 4-methylglyoxaline, which can also react as the 5-isomeride owing to virtual tautomerism, gave on methylation a mixture of the 1:4- and 1:5-dimethylglyoxalines (I and II) represented by oils which distilled at 198—199° and 224—225°.



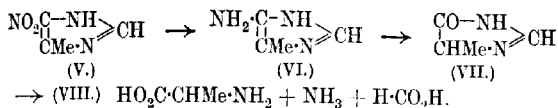
No conclusive evidence was produced at that time to show which of the two liquids was the 1:4- and which the 1:5-isomeride, but it was suggested that the base of lower boiling point was the 1:4-isomeride, since its dibromo-derivative was found, by a simple distribution method, to be more strongly basic than that of the base of higher boiling point, and it was thought that 2:5-dibromo-1:4-dimethylglyoxaline (III) would be a stronger base than 2:4-dibromo-1:5-dimethylglyoxaline (IV).



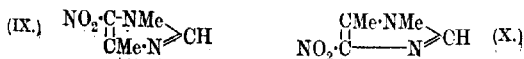
The present investigation was undertaken with the object of determining definitely the orientation of these two dimethylglyoxalines. This is important from two points of view. First, because

it has been shown (T., 1910, 97, 1814) that the base of higher boiling point is identical with the dimethylglyoxaline isolated by Jowett (T., 1903, 83, 438) from the products of distillation of *isopilocarpine* with soda-lime, and its orientation consequently forms a step in determining the constitution of *pilocarpine*. Secondly, because a study of suitable derivatives of *N*-methylglyoxaline, such as these two bases, will bring to light the properties of substituents in both the 4- and 5-positions of the glyoxaline nucleus, whereas similar study of glyoxalines containing a free imino-group furnishes information which may refer to either the 4- or 5-position owing to the operation of virtual tautomerism.

The method adopted was an examination of the reduction products of the nitro-derivatives of the two isomerides, following closely the procedure of Fargher (T., 1920, 117, 668), who showed that the reduction of 5(or 4)-nitro-4(or 5)-methylglyoxaline (V) by means of cold stannous chloride gave a small quantity of 5(or 4)-amino-4(or 5)-methylglyoxaline (VI) together with *dl*-alanine (VIII) and ammonia, a glyoxalone (VII) being assumed to be an intermediate product of the fission.

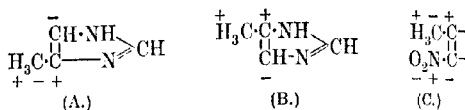


It was clear that a successful degradation of 5-nitro-1:4-dimethylglyoxaline by these means should lead ultimately to the formation of *dl*-alanine, ammonia, methylamine, and formic acid, whereas 4-nitro-1:5-dimethylglyoxaline should yield *dl*-*N*-methylalanine, ammonia (2 mols.), and formic acid. The results of the experiments have justified the view expressed previously with regard to the constitution of the dimethylglyoxalines, for it has been found that reduction of the nitro-derivative of the dimethylglyoxaline of lower boiling point gave amongst other products *dl*-alanine, whereas similar treatment of the nitro-derivative of the dimethylglyoxaline of higher boiling point gave *dl*-*N*-methylalanine. Both 1:4- and 1:5-dimethylglyoxalines are readily nitrated, and since their nitro-derivatives can also be prepared simultaneously by the methylation of 5(or 4)-nitro-4(or 5)-methylglyoxaline (V), they are 5-nitro-1:4-dimethylglyoxaline, (IX) and 4-nitro-1:5-dimethylglyoxaline (X), respectively, the latter being identical with the "nitro- $\alpha$ -*N*-dimethylimidazol" obtained by Windaus (*Ber.*, 1909, 42, 758) by nitrating the mixed dimethylglyoxalines.





The yields of the two methyl derivatives obtained by methylation of 5(or 4)-nitro-4(or 5)-methylglyoxaline differ widely, being in the proportion of 233 : 1, whereas on methylating 4(or 5)-methylglyoxaline (T., 1910, **97**, 1814) the proportions of the 1 : 4- and 1 : 5-dimethylglyoxalines, isolated in a pure state, were as 2.2 : 1, and on methylating 4(or 5)-cyanomethylglyoxaline (T., 1911, **99**, 2175) the proportions of the 1 : 4- and 1 : 5-methyl derivatives,\* isolated in a pure state, were as 2.9 : 1. The results show that glyoxalines capable of virtual tautomerism react as mixtures of the two tautomeric forms, not necessarily in equal parts, but in proportions which differ from substance to substance, and they suggest that the polarity of the substituent groups determines the condition of equilibrium. Assuming that a compound capable of virtual tautomerism would react preferentially in the form of greater homogeneous polarity (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 1), 4(or 5)-methylglyoxaline would react preferentially as A or B according to whether the negative polar effect of the tertiary nitrogen atom surpassed that of the imino-group or the reverse.



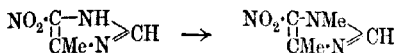
Clearly, the introduction of the strongly polar nitro-group into the ortho-position to the methyl group as in C should greatly enhance the effect of the methyl group.

It would appear from the above considerations that the glyoxaline ring may be usefully employed for comparing the polarities of substituents introduced into the 4- and 5-positions, and it is the author's intention to study for this purpose the methylation of a number of derivatives of glyoxaline.

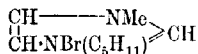
Although the results of methylation show that these glyoxalines react preferably in one of the two possible tautomeric forms, it is not possible to identify the particular form until the mechanism of the alkylation of glyoxalines is known.

If the alkylation is simply the replacement of the imino-hydrogen atom by the methyl group, then since 5-nitro-1 : 4-dimethylglyoxaline is formed preferentially, the parent compound is reacting mainly as 5-nitro-4-methylglyoxaline.

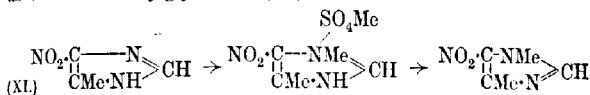
\* The constitutions of these bases and also of the methylated aminoethylglyoxalines and glyoxalineacetic acids described in the same paper follow from the determination of the constitutions of the 1 : 4- and 1 : 5-dimethylglyoxalines.



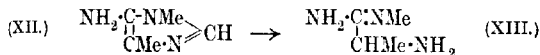
On the other hand, it is known that the combination of *N*-alkylglyoxalines with alkyl salts results in the attachment of the latter to the tertiary nitrogen atom (Pinner and Schwarz, *Ber.*, 1902, **35**, 2441), for example, *N*-methylglyoxaline combines with amyl bromide to give a quaternary salt of the formula



and it appears probable that the alkylation of glyoxalines takes a similar course, the alkyl salt attaching itself to the basic tertiary nitrogen atom. In this case, since 5-nitro-1:4-dimethylglyoxaline is formed preferentially, the parent compound is reacting mainly as 4-nitro-5-methylglyoxaline (XI).

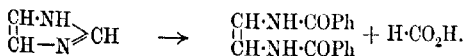


Reduction of 5-nitro-1:4-dimethylglyoxaline led to a mixture from which, besides *dl*-alanine, ammonia, and methylamine, 5-amino-1:4-dimethylglyoxaline (XII) and *dl*-alanine-*N*-methylamidine (XIII) were isolated. The constitution of the latter was



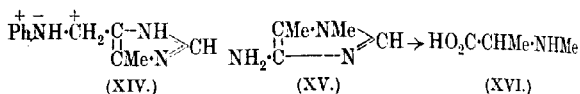
proved by hydrolysis by means of alkali, when *dl*-alanine, ammonia, and methylamine were produced in nearly the theoretical quantities.

The isolation of *dl*-alanine-*N*-methylamidine is important, for it shows that in this case at least the mechanism of the degradation of the amino-glyoxaline to the amino-acid is due, not to the intermediate formation of a glyoxalone, but to the elimination of the carbon atom in the 2-position by hydrolysis, presumably as formic acid, and therefore resembles the well-known fission of glyoxaline and 4(or 5)-alkylglyoxalines on treatment with benzoyl chloride and aqueous sodium hydroxide, which leads in the case of glyoxaline itself, for example, to dibenzoyldiaminoethylene and formic acid (Bamberger and Berl , *Ber.*, 1892, **25**, 278; Cerngross, *Ber.*, 1913, **46**, 1913).



In both reactions, the fission of the ring takes place when a negative substituent (alkyl, amino) is present in the 4(or 5)-position, and

this fact may be contrasted with a considerable amount of evidence that a positive group in the same position protects the ring from fission. Thus, 4-nitroglyoxaline (Windaus, *Ber.*, 1909, **42**, 758), glyoxaline-4-formaldhyde, methyl glyoxaline-4-carboxylate, and glyoxaline-4-carboxyanilide (Windaus, Dörries, and Jensen, *Ber.*, 1921, **54**, [B], 2745) and also derivatives of glyoxaline containing a free carboxyl group in the 4-side chain (Windaus, *Ber.*, 1910, **43**, 499) are unattacked by benzoyl chloride and sodium hydroxide, whilst 4-phenyl- and 4-*o*- and *p*-nitrophenyl-glyoxalines (Grant and Pyman, *T.*, 1921, **119**, 1893) resemble naphthiminazole (O. Fischer, *Ber.*, 1901, **34**, 930) in yielding normal *N*-benzoylglyoxalines. Possibly the failure of *N*-phenyliminobis-4:5-dimethylglyoxaline and 4-methyl-5-anilinomethylglyoxaline (XIV) (Gerngross, *Ber.*, 1919, **52**, [B], 2304) to undergo fission or even benzoylation (except as regards the imino-group in the side chain of the latter compound) under the same conditions may be attributed to the positive polarity of the carbon atom attached to the nucleus induced by the neighbouring anilino-group.



Reduction of 4-nitro-1:5-dimethylglyoxaline gave a mixture from which 4-amino-1:5-dimethylglyoxaline (XV), *dl*-*N*-methylalanine (XVI), and ammonia were isolated.

The quantities of the two aminodimethylglyoxalines isolated were very small, but sufficient to show that the amino-group in both the 4- and 5-positions has aromatic character, since both amines after diazotisation gave solutions which coupled with sodium  $\beta$ -naphthoxide, but gave no marked coloration with sodium hydroxide. In this respect their behaviour differs from that of 2-amino-glyoxaline (Pyman and L. B. Timmis, *J. Soc. Dyers and Col.*, 1922, **38**, 269). It is remarkable that both the aminodimethylglyoxalines are monacidic bases, for the corresponding secondary base, 4(or 5)-amino-5(or 4)-methylglyoxaline is diacidic (Fargher, *loc. cit.*), whereas *N*-methylglyoxaline is a stronger base than glyoxaline (Dedichen, *Ber.*, 1906, **39**, 1831).

#### EXPERIMENTAL.

##### 1:4- and 1:5-Dimethylglyoxalines.

These bases were previously prepared (T., 1910, **97**, 1814) by methylating 4-methylglyoxaline by means of methyl sulphate in alkaline solution, the 4-methylglyoxaline being prepared by Windaus

and Knoop's method (*Ber.*, 1905, **38**, 1166). Their preparation is greatly facilitated by modifying the processes in certain respects. 4-Methylglyoxaline is readily isolated in a pure state from the syrup, obtained by decomposing the crude zinc salt with hydrogen sulphide and evaporating the solution (Windaus and Knoop, *loc. cit.*), by adding anhydrous potassium carbonate, extracting with chloroform, and distilling the chloroform residue under diminished pressure.

The methylation of 4-methylglyoxaline is conveniently effected by dissolving the base in two parts of benzene, and adding methyl iodide (1 mol.). The solution gradually becomes warm and turbid, and is cooled slightly when necessary to prevent ebullition. When the vigour of the reaction has diminished, the product is heated for half an hour on the water-bath under reflux, and then the benzene is distilled off. The residue is dissolved in water, and the solution saturated with potassium carbonate and extracted with chloroform. The chloroform residue from 150 grams of 4-methylglyoxaline amounted to 100 grams, and on fractionation twice under normal pressure, using a 20-bulb rod and disk column, gave two main fractions, namely, 39 grams of 1:4-dimethylglyoxaline boiling at 198–200°, and 17 grams of the 1:5-isomeride boiling at 220–223°, besides 31 grams of fractions of intermediate boiling point. The principal fractions were converted into the nitrates, and crystallised from water, in which they are very easily soluble, when 1:4-dimethylglyoxaline nitrate formed long needles, which melted at 103–104° (corr.), and 1:5-dimethylglyoxaline nitrate formed large prisms, which melted at 128–129° (corr.).

#### *The Nitrodimethylglyoxalines.*

*A. Preparation by Nitration of the Dimethylglyoxalines.*—The nitrates of the dimethylglyoxalines were added gradually to concentrated sulphuric acid (2 c.c. to each gram), cooling slightly with water, and subsequently heating the solution for two hours on the water-bath. On diluting the solutions with water, and adding excess of sodium hydroxide, the product from the nitration of 1:5-dimethylglyoxaline gave a crystalline precipitate of the pure nitro-compound, melting at 160–161°, in a yield amounting to 83 per cent. of the theoretical, whilst the product from the nitration of the 1:4-isomeride, which gave an oil, was extracted with chloroform. On removing the solvent, nearly pure nitro-1:4-dimethylglyoxaline was obtained, in almost theoretical yield, as an oil which solidified on cooling.

*B. Preparation by the Methylation of 5-Nitro-4-methylglyoxaline.*—A mixture of 20 grams of 5-nitro-4-methylglyoxaline and 15 c.c. of methyl sulphate was heated for one hour in boiling water. The

product was dissolved in water, basified with sodium hydroxide, and extracted completely with chloroform. The alkaline solution gave on neutralisation 1.2 grams of unchanged material, melting at 248°. The chloroform residue was added to a solution of 24 grams of picric acid in 800 c.c. of hot water, when 36.0 grams of pure 5-nitro-1:4-dimethylglyoxaline picrate separated, melting at 176° (corr.), alone or mixed with the picrate of the nitration product of 1:4-dimethylglyoxaline. The mother-liquor was evaporated to low bulk, mixed with hydrochloric acid, and extracted with ether to remove picric acid. The aqueous solution was evaporated to dryness in a vacuum and moistened with water, when 0.03 gram of 4-nitro-1:5-dimethylglyoxaline, melting at 158–159°, separated. The filtrate was basified with sodium hydroxide and extracted with chloroform, which removed 0.2 gram of oil; this, after being moistened with water, deposited a further quantity of 0.03 gram, also melting at 158–159°. The total amount, 0.06 gram, was recrystallised from water, using charcoal, and gave pure 4-nitro-1:5-dimethylglyoxaline, melting at 160–161° (corr.), alone and mixed with the nitration product of 1:5-dimethylglyoxaline. The yields of the two methyl derivatives are 67.5 and 0.29 per cent. of the theoretical, respectively, allowing for the unchanged material.

*5-Nitro-1:4-dimethylglyoxaline* crystallises from ether in long, colourless, prismatic needles which melt at 57–58° (corr.). It is easily soluble in water, giving a solution alkaline to litmus. It is easily soluble in alcohol, ether, chloroform, or benzene, but very sparingly soluble in light petroleum. It boils at 155°/10 mm., but undergoes slight decomposition when distilled under normal pressure (Found: C = 42.2, 42.5; H = 5.0, 5.0; N = 30.0.  $C_5H_7O_2N_3$  requires C = 42.6; H = 5.0; N = 29.8 per cent.).

The *picrate* crystallises from water in stout, yellow needles which melt at 176° (corr.). It is sparingly soluble in hot and very sparingly soluble in cold water (approximately 1 in 1000).

*4-Nitro-1:5-dimethylglyoxaline* crystallises from water in long, colourless needles, which melt at 160–161° (corr.), and is thus identical with the "nitro- $\alpha$ -N-dimethylimidazol" of Windaus (*loc. cit.*). It is somewhat sparingly soluble in cold water, or cold organic solvents. The *picrate* crystallises from water in large, pale yellow prisms, which soften at 66° and melt at 66–69° (corr.) to a turbid liquid. It is somewhat sparingly soluble in cold water (approximately 1 in 50).

*Reduction of 5-Nitro-1:4-dimethylglyoxaline.*—Fourteen grams of the nitro-compound, melting at 57–58°, were dissolved in 50 c.c. of concentrated hydrochloric acid, and to the solution 68 grams of hydrated stannous chloride, dissolved in 150 c.c. of concentrated

hydrochloric acid, were added in the course of half an hour at  $10^{\circ}$ . The mixture was kept over-night, and filtered from a crystalline stannichloride, the filtrate being then treated with 30 grams of tin foil and evaporated to dryness. Both the crystalline tin salt and the residue were deprived of tin by hydrogen sulphide, and gave 11.0 and 5.5 grams of nearly colourless, amorphous hydrochlorides. The two fractions were mixtures containing largely the same constituents and were therefore combined. The residue, after extraction with alcohol, when 0.5 gram of ammonium chloride separated, and removal of the solvent, was added to a solution of 25 grams of picric acid in 2 litres of water, when on cooling and on concentration various deposits of pierates, at first amorphous and later crystalline, were obtained (mother-liquor from deposition of pierates, M). The amorphous pierates became partly crystalline on warming with alcohol, and the total crystalline material was subjected to a prolonged fractional crystallisation from water, when eventually 2.7 grams of 5-amino-1:4-dimethylglyoxaline pierate and 3.0 grams of *dl*-alanine-*N*-methylamidine dipicrate were isolated in a pure state. The mother-liquor M was extracted with ether to remove picric acid, evaporated to dryness, and extracted with alcohol, when 0.7 gram of ammonium chloride separated, the filtrate leaving 3.3 grams of syrupy residue. This was mixed with an excess of aqueous sodium hydroxide, and the volatile amines were distilled into hydrochloric acid. The distillate was evaporated and gave 1.3 grams of crystalline hydrochloride, of which 0.25 gram was insoluble in absolute alcohol, whilst the residue, after drying at  $100^{\circ}$ , was found to contain 54.4 per cent. of chlorine and consisted chiefly of methylamine hydrochloride ( $\text{CH}_5\text{NCl}$  requires Cl = 52.5 per cent.). The alkaline solution was acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol, which removed 1.7 grams of syrupy hydrochlorides. After removing chlorine by silver carbonate and excess of silver by means of hydrogen sulphide, the product gave 0.3 gram of crude *dl*-alanine, which melted at  $280^{\circ}$  and after two crystallisations from water melted at  $290^{\circ}$  (corr.), alone or mixed with a synthetic specimen, kindly given to the author by Dr. T. A. Henry, Director of the Wellcome Chemical Research Laboratories.

*dl*-Alanine-*N*-methylamidine dipicrate crystallises from water in yellow, elongated plates which melt and decompose at  $200^{\circ}$  (corr.). It is moderately easily soluble in hot water, but very sparingly soluble (about 1 in 625 parts) in cold water. It decomposes suddenly when heated above its melting point and proved to be unsuitable for combustion. When treated with hydrochloric acid and extracted with ether, it gave 80.3 per cent. of picric acid;  $\text{C}_4\text{H}_{11}\text{N}_3(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2$

requires picric acid = 81.9 per cent. The *dihydrochloride* was prepared from the picrate by treatment with hydrochloric acid and ether. It crystallises from water in large, colourless prisms which melt at  $242^{\circ}$  (corr.) after sintering earlier. It is anhydrous and easily soluble in water, giving a solution strongly acid to litmus, but almost insoluble in absolute alcohol (Found : C = 27.7; H = 7.5; N = 24.0.  $C_4H_{11}N_3 \cdot 2HCl$  requires C = 27.6; H = 7.5; N = 24.1 per cent.).

0.6 Gram of the *dihydrochloride* was boiled with an excess of aqueous barium hydroxide and the volatile amines were collected in aqueous hydrochloric acid. This on evaporation gave 0.40 gram of crystalline hydrochlorides, containing Cl = 57.8 per cent., the calculated yield of a mixture of methylamine hydrochloride and ammonium chloride in equimolecular proportions being 0.41 gram containing Cl = 58.6 per cent. The mixture was partly soluble in absolute alcohol, and the soluble portion was converted into the platinumchloride in two fractions which were found to contain Pt = 42.2 and 41.8 per cent., respectively :  $(NH_2Me)_2H_2PtCl_6$  requires Pt = 41.3 per cent.

The non-volatile fraction from the distillation was deprived of barium by the exact quantity of sulphuric acid and evaporated to dryness, when 0.42 gram (calc., 0.433 gram) of *dl*-alanine hydrochloride remained. This was deprived of chlorine by treatment in aqueous solution with silver carbonate, freed from traces of silver by means of hydrogen sulphide, and evaporated to low bulk, when *dl*-alanine separated in colourless prisms which melted at  $286^{\circ}$  (corr.), a specimen of the synthetic acid and a mixture of the two melting at  $287.5^{\circ}$  (corr.) in the same bath. The identity of the acid was also confirmed by analysis (Found : in substance dried at  $100^{\circ}$ , C = 40.4; H = 7.95. Calc., C = 40.4; H = 7.9 per cent.).

*Reduction of 4-Nitro-1:5-dimethylglyoxaline.*—Fourteen grams of the nitro-compound, melting at  $160$ – $161^{\circ}$ , were reduced under the same conditions as the isomeride, and worked up in the same way, except that no crystalline stannichloride separated in this case. There were thus obtained in a pure state 3.0 grams of 4-nitro-1:5-dimethylglyoxaline picrate, the mother-liquor from this yielding small quantities of other crystalline picrates, which were not obtained in a pure state, 3.4 grams of ammonium chloride, and 0.4 gram of *dl*-*N*-methylalanine. After recrystallisation from either water or strong alcohol, this substance formed prisms containing  $\frac{1}{2}H_2O$ , and on heating softened and sublimed from about  $295^{\circ}$  and effervesced, apparently being distilled, at  $307^{\circ}$  (corr.) (Found : loss at  $120^{\circ}$  = 7.8, 8.2. Calc., for  $\frac{1}{2}H_2O$ , loss = 8.0. Found, in anhydrous acid : C = 46.0; H = 8.6; N = 13.8.

Calc., C = 46.6; H = 8.7; N = 13.6 per cent.). It was easily soluble in water or hot alcohol. Its properties thus agree with the description of this acid given by Gansser (*Z. physiol. Chem.*, 1909, 61, 16).

*The Aminodimethylglyoxalines.*

5-Amino-1:4-dimethylglyoxaline picrate crystallises from water in long, stout, orange needles which darken from about 200° and melt and decompose at 209° (corr.). It is anhydrous and very sparingly soluble in cold water (Found: C = 38.5; H = 3.7; N = 24.6.  $C_5H_9N_3 \cdot C_6H_3O_7N_3$  requires C = 38.8; H = 3.5; N = 24.7 per cent.).

The hydrochloride was obtained by decomposing the picrate with hydrochloric acid and ether, when picric acid was recovered in the calculated yield. It crystallises from alcohol in greyish-white, prismatic needles, which darken from about 210° and melt to a dark red liquid at 253° (corr.) (Found, in substance dried in a vacuum over  $H_2SO_4$ : C = 40.5; H = 6.7; N = 28.7; Cl = 24.2.  $C_5H_9N_3 \cdot HCl$  requires C = 40.7; H = 6.8; N = 28.5; Cl = 24.1 per cent.).

This salt dissolves in 20 per cent. aqueous sodium hydroxide, giving a clear solution which quickly deposits colourless plates melting at about 155°. This substance—presumably the corresponding base—is easily soluble in water, or alcohol, but sparingly soluble in ether. It crystallises from alcohol in diamond-shaped plates, which melt at 160°.

4-Amino-1:5-dimethylglyoxaline picrate crystallises from water in brownish-yellow plates which darken from about 180° and melt and decompose at 220° (corr.). It is anhydrous and very sparingly soluble in cold water (Found: C = 38.6; H = 3.6; N = 25.3.  $C_5H_9N_3 \cdot C_6H_3O_7N_3$  requires C = 38.8; H = 3.5; N = 24.7 per cent.).

The hydrochloride was obtained by decomposing the picrate with hydrochloric acid and ether, when picric acid was recovered in the calculated yield. It crystallises from absolute alcohol in greyish-white spikes, which darken from about 195° and melt at 225° (corr.) (Found, in substance dried in a vacuum over  $H_2SO_4$ : C = 40.4; H = 6.7; N = 28.6; Cl = 24.3.  $C_5H_9N_3 \cdot HCl$  requires C = 40.7; H = 6.8; N = 28.5; Cl = 24.1 per cent.). This salt dissolves in 20 per cent. aqueous sodium hydroxide, giving a clear solution which slowly deposits small prisms, which melt at about 85° and probably represent the corresponding base.

The hydrochlorides of 5-amino-1:4-dimethylglyoxaline (A) and 4-amino-1:5-dimethylglyoxaline (B) are readily soluble in water, giving solutions neutral to litmus, fairly readily soluble in hot, but



sparingly soluble in cold absolute alcohol. After treatment with hydrochloric acid and sodium nitrite, both amines give colourless solutions which yield with sodium hydroxide only faintly yellow solutions, but give on addition to aqueous sodium  $\beta$ -naphthoxide as to A a clear cherry-red solution, and as to B a sparingly soluble orange dye. On treatment with aqueous sodium acetate and benzaldehyde, B gives a crystalline benzylidene derivative, whilst A apparently also forms a benzylidene derivative, although this did not crystallise. Hot (but not cold) ammoniacal silver nitrate is reduced by both amines. Neither amine gives a coloration with cold ferric chloride, but on warming the solutions A turns yellow and B shows no change. On adding aqueous sodium hydroxide to solutions of the amines containing sodium nitroprusside, A gives an immediate brownish-yellow colour, whilst B gradually develops a lemon-yellow colour.

The author is indebted to Mr. I. E. Balaban, M.Sc.Tech., for carrying out the analyses recorded in this paper.

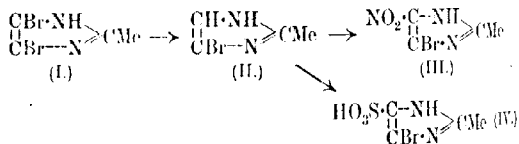
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UNIVERSITY OF MANCHESTER.

[Received, October 21st, 1922.]

### CCCXVI.—Bromo-derivatives of 2-Methylglyoxaline.

By LOUIS LIGHT and FRANK LEE PYMAN.

THE bromination of 2-methylglyoxaline has been studied previously by Radziszewski (*Ber.*, 1882, **15**, 2707), who isolated a product which he regarded as tribromo-2-methylglyoxaline. This is now shown to be the hydrobromide of 4:5-dibromo-2-methylglyoxaline (I). On reducing this base with aqueous sodium sulphite in excess, 4-bromo-2-methylglyoxaline (II) results, and this yields on nitration 4-bromo-5-nitro-2-methylglyoxaline (III), and on sulphonation 4-bromo-2-methylglyoxaline-5-sulphonic acid (IV).



The behaviour of the mono- and di-bromo-derivatives of 2-methylglyoxaline is thus similar to that of 4-bromo- and 4:5-dibromoglyoxalines (Balaban and Pyman, this vol., p. 947).

## EXPERIMENTAL.

## 4 : 5-Dibromo-2-methylglyoxaline.

Ten grams of 2-methylglyoxaline in 60 c.c. of chloroform were treated with a solution of 40 grams of bromine in chloroform at  $-5^{\circ}$  to  $0^{\circ}$ . The product was distilled with steam to remove chloroform and excess of bromine, and the resulting aqueous solution was kept, when 9.7 grams of dibromo-2-methylglyoxaline hydrobromide separated. On concentration, a further quantity of 1.4 grams of the same salt separated, the two crops yielding 7.7 grams of the base on treatment with hot water and a limited quantity of sodium carbonate; the yield is thus 26 per cent. of the theoretical.

The mother-liquors on distillation with sodium carbonate gave ammonia in a yield of 22 per cent. of the theoretical, but apart from a little oxalic acid and a trace of unchanged 2-methylglyoxaline, no crystalline by-products of the reaction could be isolated.

4 : 5-Dibromo-2-methylglyoxaline crystallises from 40 per cent. aqueous alcohol in long, silky needles, which sinter and darken at about  $236^{\circ}$  and melt at  $239-240^{\circ}$  (corr.) to a dark brown liquid (Found : C = 20.1; H = 1.9; N = 11.8; Br = 66.0.  $C_4H_5N_2Br_2$  requires C = 20.0; H = 1.7; N = 11.7; Br = 66.6 per cent.).

It is soluble in about 350 parts of boiling water, almost insoluble in cold water, giving a solution neutral to litmus, easily soluble in alcohol, acetone, ethyl acetate, or glacial acetic acid, fairly easily soluble in ether, but very sparingly soluble in chloroform, benzene, or light petroleum. It is soluble in cold aqueous sodium hydroxide or strong aqueous ammonia, but not in aqueous sodium carbonate.

The hydrochloride and hydrobromide were obtained by dissolving the base in warm 5N-solutions of the corresponding acids, and allowing the solutions to cool, when they separated in irregular, prismatic needles, which charred at about  $255^{\circ}$  and  $280^{\circ}$ , respectively. Both salts dissociate on the addition of water, giving the base.

Radziszewski's "Tribromo-2-methyl-glyoxaline."—By the action of bromine on 2-methylglyoxaline in aqueous solution, Radziszewski (*loc. cit.*) obtained a white precipitate, which crystallised well from alcohol, melted at  $258^{\circ}$ , and contained Br = 74.9 per cent. He regarded this compound as tribromo-2-methylglyoxaline, which requires Br = 75.2 per cent., but repetition of his experiment has shown that this product is 4 : 5-dibromo-2-methylglyoxaline hydrobromide, which requires Br = 74.8 per cent., for it had no definite melting point, but charred at about  $280^{\circ}$ , and was dissociated on the addition of water, giving the base 4 : 5-dibromo-2-methylglyoxaline, which melted at  $239-240^{\circ}$  (corr.), alone or mixed with the substance prepared as described above.

Another tribromo-2-alkylglyoxaline is described by Radziszewski and Szul (*Ber.*, 1884, 17, 1291), who record the formation of di- and tri-bromo-derivatives by the bromination of 2-isobutylglyoxaline; their description of the tribromo-derivative, however, makes it quite clear that this is the hydrobromide of the dibromo-compound, 4 : 5-dibromo-2-isobutylglyoxaline.

*Reduction of 4 : 5-Dibromo-2-methylglyoxaline by Sodium Sulphite*.—When the dibromo-compound is boiled with 20 per cent. aqueous sodium sulphite, it is reduced to 4-bromo-2-methylglyoxaline, and no by-product of the reaction has been observed. When one molecular proportion of sulphite was employed, the monobromo-derivative was obtained in a yield of only 23 per cent. of the theoretical after boiling for seven hours, a large amount of the dibromo-compound remaining unchanged, and in order to complete the conversion it was necessary to employ a large excess of sulphite. Five grams of the dibromo-compound were boiled with 25 grams (5 mols.) of hydrated sodium sulphite in 20 per cent. aqueous solution for six hours under reflux. On cooling the clear solution, 1.9 grams of the monobromo-compound crystallised out, and a further quantity of 0.8 gram was obtained by extraction with ether. The yield thus amounts to 82 per cent. of the theoretical, and the product was nearly pure, melting at 159–161°. It was purified by conversion into the pierate and crystallisation of this salt from water.

#### 4-Bromo-2-methylglyoxaline.

4-Bromo-2-methylglyoxaline crystallises from water in short, stout rods or from chloroform in elongated plates, which melt at 162–163° (corr.). It is soluble in about 10 parts of boiling water, giving a solution feebly alkaline to litmus, somewhat sparingly soluble in cold water, very readily soluble in alcohol, ethyl acetate, or acetone, readily soluble in ether, fairly readily soluble in chloroform or benzene, and almost insoluble in hot light petroleum. It is readily soluble in dilute mineral acids or sodium hydroxide, and more soluble in aqueous ammonia than in water, but not so in aqueous sodium carbonate. It gives a clear cherry-red solution with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate (Found : C = 29.4; H = 3.4; N = 17.0; Br = 49.4.  $C_4H_5N_2Br$  requires C = 29.8; H = 3.1; N = 17.4; Br = 49.6 per cent.).

The *hydrochloride* crystallises from 5*N*-hydrochloric acid in colourless, quadrilateral plates, which contain  $1H_2O$  and after drying at 100° melt at 187–188° (corr.). It is readily soluble in water, giving a solution strongly acid to litmus, but is sparingly soluble in cold hydrochloric acid (Found : in air-dried salt. C = 22.0; H = 3.7; N = 13.4; Cl = 16.5; loss at 110° = 8.8

$C_4H_5N_2Br \cdot HCl \cdot H_2O$  requires C = 22.3; H = 3.7; N = 13.0; Cl = 16.5;  $H_2O$  = 8.4 per cent.).

The *nitrate* crystallises from water in silky needles which are anhydrous and melt and decompose at  $132^\circ$  (corr.) It is easily soluble in water or alcohol (Found: C = 21.8; H = 2.5.  $C_4H_5N_2Br \cdot HNO_3$  requires C = 21.4; H = 2.7 per cent.).

The *picrate* crystallises from water in yellow, prismatic needles, which melt at  $161$ – $163^\circ$  (corr.). It is easily soluble in hot and sparingly soluble in cold water (Found: C = 30.8; H = 2.4; N = 18.1.  $C_4H_5N_2Br \cdot C_6H_3O_7N_3$  requires C = 30.8; H = 2.1; N = 17.9 per cent.).

*Nitration of 4-Bromo-2-methylglyoxaline.*—Three grams of 4-bromo-2-methylglyoxaline nitrate were added to 6 c.c. of concentrated sulphuric acid, and the solution heated for two hours in a water-bath. After diluting it with water, and neutralising the greater part of the acid with sodium hydroxide, 2.25 grams of the pure nitro-compound were collected, that is, 82 per cent. of the theoretical yield.

*4-Bromo-5-nitro-2-methylglyoxaline* crystallises from water in small, colourless needles and from alcohol or glacial acetic acid in plates which melt and decompose at  $268^\circ$  (corr.) after previous sintering (Found: C = 23.1; H = 2.3; Br = 38.4.  $C_4H_4O_2N_3Br$  requires C = 23.3; H = 1.9; Br = 38.8 per cent.). It is sparingly soluble in boiling water, and almost insoluble in cold water, easily soluble in hot alcohol or hot glacial acetic acid, but almost insoluble in ether, chloroform, or benzene. It is soluble in 5*N*-hydrochloric acid, giving a colourless solution, from which it is precipitated on dilution with water, and dissolves readily in aqueous sodium hydroxide, sodium carbonate, or ammonia, giving yellow solutions. On exposure to bright sunlight, it becomes pale green in colour, and thus resembles 5-nitro-4-methylglyoxaline (Windaus, *Ber.*, 1909, 42, 758) and 4-*o*-nitrophenylglyoxaline (Grant and Pyman, *F.*, 1921, 119, 1893).

*Sulphonation of 4-Bromo-2-methylglyoxaline.*—Two grams of 4-bromo-2-methylglyoxaline were converted into the sulphate by the addition of 3 c.c. of sulphuric acid, 10 c.c. of 70 per cent. oleum were added, and the mixture was heated under reflux for three hours at  $150$ – $160^\circ$ . The product was poured on to ice, when 2.3 grams of practically pure sulphonic acid separated, that is, 83 per cent. of the theoretical yield.

*4-Bromo-2-methylglyoxaline-5-sulphonic acid* crystallises from water in elongated prisms which sinter and darken from about  $155^\circ$  and melt and decompose at  $266\frac{1}{2}^\circ$  (corr.). It contains  $1H_2O$ , which is not lost at  $120^\circ$ . It is soluble in about 14 parts of boiling

water and in more than 100 parts of cold water. It is very sparingly soluble in absolute alcohol (Found: C = 18.4, 18.5; H = 2.7, 2.8; Br = 30.9.  $C_4H_5O_3N_2BrS.H_2O$  requires C = 18.5; H = 2.7; Br = 30.9 per cent.).

*Hydrolysis*.—0.5 Gram of the sulphonic acid was heated with 5 c.c. of 36 per cent. sulphuric acid for three hours at 170°. On basifying the solution, 0.17 gram of pure 4-bromo-2-methylglyoxaline separated.

The authors are indebted to the Wellcome Chemical Research Laboratories for a part of the 2-methylglyoxaline employed in this investigation.

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### CCCXVII.—*Action of Ammonium Nitrate and of Aqueous Ammonia on Copper. Properties of Cupric Tetrammine Nitrite and Nitrate.*

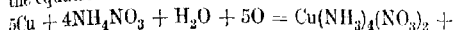
By HENRY BASSETT and REGINALD GRAHAM DURRANT.

THAT solutions of ammonia or ammonium salts rapidly attack copper is well known. The case of the attack by ammonium nitrate in aqueous solution assumed considerable interest in connexion with the use of copper or alloys of copper in the manufacture of ammunition. When these were used in conjunction with high explosives containing ammonium nitrate, corrosion was liable to occur sooner or later whenever absorption of moisture by the explosive allowed aqueous exudations therefrom to come into contact with the copper or copper alloy. Such corrosion rarely occurred except in situations where some air at least was present, indicating that atmospheric oxygen was essential to the process, as is normally the case in the corrosion of metals by salt solutions. Striking dark blue and green products, resulting from contact of ammonium nitrate with copper, immediately directed attention to the action. It became necessary to examine these products, as indeed many others, to see whether they were likely to prove dangerous or harmful. Into the full details of this aspect of the matter it is not necessary to enter, but a few points bearing on the chemistry of copper are now recorded.

It was at once recognised that the dark blue, prismatic crystals formed in the corrosion of copper by ammonium nitrate consisted of cupric tetrammine nitrate,  $Cu(NH_3)_4(NO_3)_2$ , whilst the green sub-

stance also present was the basic nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ . Both of these are well-known compounds and can readily be prepared in a pure state. The corrosion products also contained small amounts of other substances, notably of nitrite, and the main interest from the chemical point of view centred round the question as to the form in which this was present.

Although not giving a true picture of the course of the reaction, the equation



$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$  probably represents fairly well the net result of the main reactions occurring between copper and ammonium nitrate in presence of air and water. The products of corrosion actually found in practice do not as a rule contain the basic nitrate and the tetrammine in equimolecular proportions, and this for two reasons: First, because the concentrated solution of the highly soluble tetrammine nitrate is separated, by diffusion and by capillary action, from the basic nitrate, which is deposited in the solid state; secondly, because hydrolysis occurs in situations where the tetrammine is exposed to moist air and causes it slowly to revert to the basic nitrate with loss of ammonia. Thus it was often noticed that a green crust of the basic nitrate was in contact with the metal, the blue tetrammine deposit overlying it, but in some cases the latter deposit was separated by some distance from the former. Where the corrosion occurs in presence of much water, the blue tetrammine may never be in a condition to separate in the solid state and is ultimately converted entirely into the basic nitrate. Analyses I and II illustrate the sort of corrosion products met with in practice. Corrosion I consisted chiefly of deep blue, prismatic crystals mixed with a moderate amount of green material. It was obtained from a piece of ammunition filled with 40/60 amatol. When this munition was first opened for the purpose of sampling the filling, there was no corrosion, but when next opened, in three weeks' time, much corrosion was found on those parts of the copper where amatol had been scattered during excavation of the sample. The lead present is derived from solder. The corrosion was washed with acetone before analysis in order to remove any trinitrotoluene.

Corrosion II, which consisted almost entirely of dark blue crystals, was obtained from the top of a tinned copper can on which a bag of ammonium nitrate had been lying for several weeks.

	CuO.	PbO.	SnO <sub>2</sub> .	NH <sub>3</sub> .	N <sub>2</sub> O <sub>5</sub> .	N <sub>2</sub> O <sub>3</sub> .	H <sub>2</sub> O and loss, etc. (by diff.).
I.	35.6	2.1	trace	16.6	32.0	1.9	11.8 per cent.
II.	30.8	—	0.9	21.9	38.8	0.5	7.1 per cent.

No. II contained more than 80 per cent. of the tetrammine; a trace of carbonate was also present.

*Action of Ammonium Nitrate Solution on Copper.*

When fine copper gauze is immersed in a saturated solution of ammonium nitrate with free access of air at the ordinary temperature, the solution acquires a blue colour in a very short time and after about twenty-four hours a green solid begins to separate. If too much gauze has not been used, the metal will have completely disappeared in about a fortnight and there will be a copious green precipitate in a deep blue solution. The green solid, after filtration and washing with cold water, is found to be identical in composition and behaviour with the basic nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ , prepared by heating a solution of copper nitrate to which sodium nitrite has been added (see Dammer, "Handbuch der anorganischen Chemie," II, 2, 716). If portions of solid ammonium nitrate crystals or copper gauze projected above the solution, capillary action and subsequent evaporation gave rise to the formation of blue crystals,  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ , identical with those obtained in the usual way and also with those obtained in corrosions I and II.

Cupric tetrammine nitrate, when quite dry, is remarkably stable. On heating in a dry tube, it melts at about  $210^\circ$ , bubbles rapidly for a while, and then explodes vigorously at about  $212^\circ$ , leaving a residue of black cupric oxide. If any basic nitrate is present in the tetrammine, melting seems to begin at a much lower temperature, even as low as  $150^\circ$ , owing no doubt to some solution being formed from the water contained in the basic salt. At  $120^\circ$  in a vacuum, the tendency of the dry tetrammine to lose ammonia is negligible, and even after heating for two hours at  $160$ – $190^\circ$  in a current of dry air the total loss of ammonia was only 3.16 per cent. or less than one-eighth of the total amount present. In moist air, even at the ordinary temperature, the salt is slowly hydrolysed with formation of the basic nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ .

*The Corrosion of Copper by Aqueous Ammonia.*

The mechanism of the reaction which gives rise to the nitrite in the corrosion of copper by ammonium nitrate is of interest. From our investigations we have come to the conclusion that little or no reduction from nitrate to nitrite is brought about by copper under the above conditions,\* but that the nitrite is produced by the oxida-

\* *Spongy* copper can slowly reduce alkaline nitrate solutions to nitrite in absence of air (Müller and Weber, *Z. Elektrochem.*, 1903, 9, 965) and we have found that this also applies to solutions of ordinary neutral ammonium nitrate.

tion of ammonia (resulting from hydrolysis of the tetrammine nitrate) in presence of copper, which acts as a positive catalyst. Thus, when copper was left in 2*N*- and in 8*N*-ammonia in absence of nitrate but exposed to the air, considerable quantities of nitrite were formed which obviously resulted from atmospheric oxidation; 25 and 23.9 molecules of CuO were formed in the two experiments for each molecule of  $N_2O_3$ ; which seems, on the whole, to indicate that the oxidation of the ammonia is merely catalysed by the copper or copper salts and is not directly "coupled" with the oxidation of the copper.

The precise course of events in the corrosion of copper gauze by solutions of ammonia depends on several rather ill-defined factors. The first solid product of the reaction is normally cupric hydroxide (loss on ignition—found 18.6 per cent.; calc. 18.4 per cent.), which begins to change into the oxide in the course of a few days. When this occurs, corrosion proceeds comparatively rapidly. In other cases, owing to the intervention of atmospheric carbon dioxide, a very compact and adherent coating of malachite,  $CuCO_3 \cdot Cu(OH)_2$ , is formed which protects the copper from further attack far more effectively than does the cupric oxide. When this occurs, corrosion proceeds very slowly. Whether the malachite is the first product formed or whether it is preceded by a small amount of the hydroxide, which later on becomes carbonated, is undecided. We have obtained corrosion products containing nearly 98 per cent. of malachite by leaving copper gauze and 2*N*-ammonia exposed to the air. The relative proportions of the copper and ammonia oxidised in the two cases do not seem to differ greatly.

The compositions of the blue solutions formed also differ in the two cases. When cupric oxide has formed and corrosion been rapid, about half the copper in solution is present as cupric tetrammine nitrite and half as cupric diammine carbonate. When, however, malachite has formed and corrosion has been slow, most of the copper in solution is present as the diammine carbonate and only about 5 per cent. as the tetrammine nitrite. It is evident, therefore, that atmospheric carbon dioxide plays an important part in the changes which occur when copper and ammonia are exposed to the air.

Péligot (*Compt. rend.*, 1861, 53, 209) showed that a vigorous reaction occurred between strong ammonia solution, finely divided copper, and air with formation of ammonium nitrite, oxides of copper, and a blue solution.\* By evaporating the blue solution to

\* We also find that ammonia acts vigorously on finely divided copper (reduced from solution by means of zinc). After nine days, no metallic copper remained and all blue tetrammine salts originally formed had separated.



dryness on the water-bath and extracting with hot alcohol saturated with ammonia, he isolated violet-blue crystals, to which, merely on the strength of a copper estimation, he assigned the formula  $\text{Cu}(\text{NO}_2)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ . It has been conclusively shown that these violet-blue crystals consist of cupric tetrammine nitrite and several alternative methods of preparing this compound have been worked out. As will be seen, the most satisfactory method (III) involves the previous preparation of van der Meulen's basic nitrite, a salt exactly analogous to the basic nitrate. Since the present paper was written, the formation of nitrite during the action of air and ammonia on copper has been noticed by Joyner (this vol., p. 1513).

#### *Preparation of Cupric Tetrammine Nitrite.*

The five methods employed are given in Roman numerals, which appear also at the head of the analysis columns referring thereto.

*Method I. A Modification of Pélégot's Method, Gauze replacing finely divided Copper.*—The blue solution obtained by the combined action of aqueous ammonia and air on gauze was evaporated to dryness in a warm cupboard and the residue extracted several times on the water-bath with alcohol previously saturated with ammonia gas. The extraction must be done rapidly or otherwise all the ammonia is driven off and very little copper salt dissolves. The hot alcoholic extract was rapidly filtered and on cooling deposited deep blue crystals, which were filtered with suction and air-dried. During drying, they became more purple as though slight superficial decomposition had occurred. The yield by this method is poor; only 0.4 gram of the blue crystals was obtained from the corrosion of 6 grams of copper gauze. This was doubtless due to decomposition of ammonium nitrite during the evaporation of the original aqueous solution or during extraction with hot alcoholic ammonia.

*Methods II and III. From the Basic Nitrite,  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ .*—Since Pélégot's method gives very poor yields and involves the preliminary preparation of a somewhat indefinite mixture, it seemed simpler to deal with the definite compound,  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ , first prepared by van der Meulen (*Ber.*, 1879, 12, 758). Method II was to extract from this compound with alcoholic ammonia as in

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ated from the solution as basic salts. Analysis of the green solid product corresponded with a mixture of  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$  (1.5),  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$  (3.0),  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (51.5), and  $\text{Cu}(\text{OH})_2$  (44.0 per cent.).

This would be the kind of mixture which Pélégot extracted with alcoholic ammonia, and it seems probable that the ammine nitrite he obtained was contaminated with nitrate. We have only observed the formation of nitrate when using the finely divided reduced copper. With copper gauze, the oxidation of ammonia seems to proceed only as far as nitrous acid.

Péligot's method, and method III to extract with aqueous ammonia (*d* 0.880).

Method II is somewhat tedious, as repeated extraction is necessary. Several grams of cupric tetrammine nitrite were prepared in this way and dried over a mixture of calcium chloride and its hexammine to minimise decomposition. As, however, the yield by this method was only 40 per cent. of the theoretical, and the extracted residue was practically free from nitrite, it is clear that considerable decomposition of nitrite occurs in this process.

Method III gives excellent results and we recommend it for the preparation of the tetrammine nitrite in quantity. The readily prepared basic nitrite is treated with the minimum amount of ammonia (*d* 0.880) at the ordinary temperature, the deep blue solution filtered through asbestos from black cupric oxide, and allowed to evaporate and crystallise at the ordinary temperature over quicklime to which a few drops of ammonia (*d* 0.880) have been added. If less than the theoretical amount of ammonia is used, the pure salt may be obtained after one evaporation, but the yield will be smaller (IIIa gives the analysis). The theoretical yield may be very nearly reached by using rather more ammonia, but this extraction will deposit a dark stain on the dish when evaporation has nearly finished, and the resulting crystals must be redissolved in a small quantity of ammonia and the solution again evaporated—possibly the operation may have to be repeated (IIIb gives the analysis).

Two more direct methods were attempted:

*Method IV.*—The action of strong ammonium nitrite solution containing excess of ammonia on cupric hydroxide.

*Method V.*—The action of the gases, evolved from arsenious oxide and nitric acid, on cupric hydroxide suspended in ammonia (*d* 0.880). Blue solutions were obtained in both cases which on evaporation over quicklime yielded deep blue crystals. These were invariably a mixture (apparently mixed crystals) of cupric tetrammine nitrite and nitrate and it does not appear possible to obtain the pure nitrite by these methods.

*Analyses of Preparations Obtained by the Foregoing Five Methods.*

The nitrite was estimated by standard permanganate, ammonia by distillation with sodium hydroxide into standard acid, any nitrate by further distillation after reduction over-night with Devarda's alloy, the amount of nitrate being calculated from the excess of ammonia over that due to reduction of nitrite. The copper was either precipitated and weighed as oxide or estimated by Rose's method.

	Percentages found by methods						Calculated.	
	I.	II.	III.		IV.	V.	Péligot's formula.	$\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$
			a.	b.				
$\text{CuO}$ .....	39.4	37.2	35.5	35.9	33.4	35.7	35.4	35.6
$\text{NH}_3$ .....	26.0	27.9	30.3	30.3	27.9	29.8	15.2	30.4
$\text{N}_2\text{O}_5$ .....	32.9	33.8	33.8	33.9	17.8	29.9	33.8	34.0
$\text{N}_2\text{O}_3$ .....	not determined		none	none	20.7	4.1		
$\text{H}_2\text{O}$ (diff.)	1.7	1.1					15.6	
	100.0	100.0	99.6	100.1	99.8	99.5	100.0	100.0

The figures for I and II correspond approximately with the presence of 13 and 8 per cent., respectively, of basic nitrite,  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ , probably formed by hydrolysis and decomposition during crystallisation of the hot solutions. It is also probable that some cupric diammine nitrite was formed at these comparatively high temperatures, as indicated by the purple coating observed on the crystals (this diammine nitrite is described later on). IV and V correspond with mixtures of the tetrammine nitrite with 47.8 and 9.8 per cent., respectively, of the tetrammine nitrate. The deficit in IIIa must have been due to a trace of water retained by the crystals. If allowance is made for this, the agreement is excellent. The slight excess of copper in IIIb was due to a trace of cupric oxide still held in the crystals and corresponding to 0.34 per cent. It is to be noted that the recrystallisations of this specimen had extended over two months. There was no nitrate, however, showing that no auto-oxidation or atmospheric oxidation had occurred. It will be noticed that the ammonia content calculated from Péligot's formula is just half what was found in IIIa and IIIb, and is much less than the amount found in any of the other specimens.

#### *Properties of Cupric Tetrammine Nitrite.*

As Péligot described it, this salt forms needle-shaped prisms of a beautiful violet-blue colour. We have obtained crystals more than 1 cm. in length by slow deposition from aqueous ammonia. The pure salt is exceedingly soluble in water and yields a perfectly clear, dark blue solution. This becomes a test of purity as regards contaminating hydroxide. A specimen proved to contain 6.5 per cent. of hydroxide immediately gave a pale blue deposit on the addition of a few drops of water. A deposit occurs slowly when excess of water is added to the pure salt, but if a little ammonia is then added the solution becomes and remains perfectly clear. Such solutions were used in the nitrite estimations and were slowly delivered from the burette into standard permanganate, previously warmed with excess of sulphuric acid. The dry salt, when slowly heated, first gives off ammonia, later on it evolves red fumes accom-

panied by steam and leaves a residue of cupric oxide. This reaction appears to have afforded the only estimation in Pélégot's analysis. His percentage of CuO agrees with the formula  $\text{Cu}(\text{NO}_2)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , but almost equally well with the formula  $\text{Cu}(\text{NO}_2)_2 \cdot 4\text{NH}_3$ . He found it necessary to mix the powdered salt with silica in order to avoid explosion. We find that the pure salt may be heated either slowly or rapidly without any explosion, but all specimens containing nitrate are apt to explode towards the end of the heating process. The action of heat on pure cupric tetrammine nitrate has been recorded in this paper. The explosion at  $212^\circ$  was so vigorous that the apparatus was broken; the loss of ammonia after two hours at  $200^\circ$  in a continuous current of air was only 3 per cent., whereas the corresponding nitrite loses more than 15 per cent. at temperatures below  $100^\circ$ , and this without any current of air. It appears, therefore, that ammonia is held firmly in the nitrate, but not in the nitrite, and that in mixtures the nitrite is quietly decomposed by heat, final explosion being due to subsequent action on the nitrate.

*Cupric Diammine Nitrite,  $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ .*

This derivative was obtained as a purple powder by heating finely powdered blue tetrammine nitrite for twenty-four hours at  $97^\circ$  in a tube provided with a loose glass stopper. The percentage losses per time were :

Hours .....	1.3	2.3	3.55	4.8	6.8	9.3
Per cent. loss .....	3.37	4.9	7.12	8.5	10.56	11.56
Hours .....	12.9	16.5	19.7	21.9	23.9	
Per cent. loss .....	13.17	13.7	14.54	15.58	15.58	

These figures present an asymptotic curve.

The loss calculated for removal of  $2\text{NH}_3$  is 15.2 per cent. The extra 0.38 per cent. must have been due to some absorption of moisture during the process of powdering and transference to the tube.

This purple powder readily dissolves in ammonia to form a perfectly clear blue solution, and on exposing the powder to an atmosphere containing dry ammonia at the ordinary temperature, the violet-blue tetrammine nitrite was re-formed.

*The Effect of Moist Air on Cupric Tetrammine Nitrite.*

A finely powdered sample of the tetrammine nitrite, protected from dust, was exposed to moist air for about three months. The dry grey powder was then analysed, with the following percentage results :

$\text{CuO}$  48.23;  $\text{N}_2\text{O}_5$  35.28;  $\text{NH}_3$  14.49;  $\text{H}_2\text{O}$  (by diff.) 2.00.  
45\*

These figures correspond very closely with those required by a mixture of 80 per cent. of cupric diammine nitrite,  $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ , and 20 per cent. of the basic nitrite,  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ . It appears, therefore, that in moist air the tetrammine nitrite loses half its ammonia, yielding the diammine nitrite, which then very slowly gives place to the basic nitrite through hydrolysis. No nitrate had been formed.

*Preparation of van der Meulen's Basic Nitrite,  $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ .*

The method of preparation (van der Meulen, *loc. cit.*) is to add alcohol to an aqueous solution containing equivalent amounts of copper sulphate and potassium nitrite. After filtering from the heavy precipitate, the dark green alcoholic solution is evaporated on the water-bath until nearly colourless. Alcohol and ethyl nitrite are given off and the basic nitrite separates as a bluish-green, crystalline deposit. The best yield obtainable seems to be about half the theoretical, but it is often half that, and experiments were made to find the best conditions for a good yield and also to examine the nature of the products formed, as the information given by van der Meulen on these points is rather vague. The best results were obtained when the temperature during the first stage in the preparation was kept below  $15^\circ$ . At temperatures exceeding this, there is considerable loss of ethyl nitrite during the addition of alcohol. The proportion of alcohol to water should be in the ratio 5:4 by volume at least. The precipitate formed on the addition of alcohol is of a complex nature and its composition varies considerably with the temperature, proportion of alcohol added, lapse of time between precipitation and filtration, etc. Of the total, air-dried solid, from 50 to 60 per cent. consists of potassium sulphate and more than 10 per cent. may consist of the double sulphate,  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ , which is often obtained as large, green crystals, especially if some time has been allowed to elapse before filtration; otherwise, copper sulphate pentahydrate, with no double sulphate, appears to be formed. Cupric hydroxide is always present, sometimes apparently as such (exceeding 11 per cent.), but in other cases only in the form of basic copper sulphate. Lastly, the air-dried solid contains 0.7 per cent. or less of cupric nitrite, probably as basic nitrite.

It is of course owing to this co-precipitation of copper salts with potassium sulphate that the yield of basic nitrite is so poor.

The final filtrate from which the basic copper nitrite crystallises still contains from 20 to 24 per cent. of the original potassium nitrite and a trace—or sometimes more—of copper. This trace of copper nevertheless imparts a strong green colour to the solution, and migration experiments proved that it is present as a complex anion—



University College, Reading, and the authors wish to express their thanks to the Director of Artillery for permission to publish the results.

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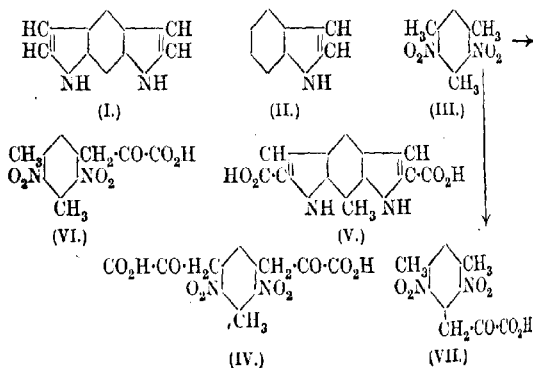
[Received, September 8th, 1922.]

### CCCXVIII.—The Synthesis of *m*- $\alpha$ -Benzbispyrrole Derivatives.

By WILLIAM DAVIES and EDGAR HERBERT CUTHBERT HICKOX.

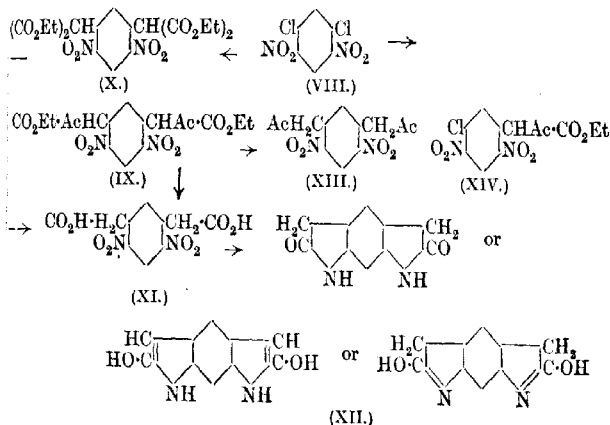
A SURVEY of the formulæ of many complicated natural products shows that they are often constituted by the linking of simple cyclic substances either by means of one or more side chains, or by having one or more atoms in common. It is therefore of some interest to study the preparation and properties of new cyclic systems which should, from analogy with simpler naturally occurring systems, be found in nature. The preparation of derivatives of *m*- $\alpha$ -benzbispyrrole (I), which, from its structural similarity to indole (II), should be the product of vital syntheses, has accordingly been carried out.

The line of attack first adopted, which we owe to the kindness of Professor W. H. Perkin, F.R.S., was to condense dinitromesitylene (III) with ethyl oxalate and sodium ethoxide after the method of Reissert (*Ber.*, 1897, 30, 1030; also see Kermack, Perkin, and Robinson, T., 1921, 119, 1625) in order to produce the dinitrotolylene-dipyrvic acid (IV), which should be converted by reduction into methyl-*m*- $\alpha$ -benzbispyrrole-dicarboxylic acid (V), and thence, by



elimination of two molecules of carbon dioxide, into 8-methyl-*m*- $\alpha$ -benzbispyrrole itself. Unfortunately, the condensation could only be effected between one methyl group and ethyl oxalate, and insufficient is known of the effects of steric hindrance, which is probably here called into play, to decide definitely which of the two formulæ (VI and VII) represents the *dinitro-m-xylylpyruvic acid* actually produced. The two methyl groups in 4:6-dinitro-*m*-xylene also could not be condensed smoothly with ethyl oxalate and sodium ethoxide. In both condensations the use of higher temperatures in the attempt to introduce two pyruvic ester groups into the molecule resulted in the decomposition of the monopyruvic ester first formed.

The successful method adopted is one involving some interesting theoretical considerations. It is based on the replacement of both chlorine atoms in 1:3-dichloro-4:6-dinitrobenzene (VIII) by ethyl acetoacetate or malonate ester groupings, when (IX) and (X), respectively, are formed. These substances can be converted into 4:6-dinitrophenylene-1:3-diacetic acid (XI), which by suitable reduction can be transformed into the desired 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole (XII) or the two other tautomerides indicated. It is to be expected that 4:6-dinitro-1:3-diacetylbenzene (XIII), obtained from (IX), will also be converted into a benzbispyrrole derivative by similar means, but this has not yet been carried out.



This scheme was evolved before it was known that Borsche and Bahr (*Annalen*, 1913, **402**, 100, 106) had condensed the sodium compounds of ethyl acetoacetate and ethyl malonate with 1:3-



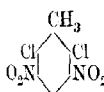
dichloro-4 : 6-dinitrobenzene. They found that, after the substitution of one acetoacetic or malonic ester group for one chlorine atom, the second chlorine atom was very difficult to replace. For example, whilst ethyl 5-chloro-2 : 4-dinitrophenylacetoacetate (XIV) can be isolated in a yield of about 80 per cent. in four hours by carrying out the condensation in ether, a large amount of (XIV) still remains when (VIII) is condensed with excess of ethyl sodioacetoacetate under the same conditions for a period of two hundred and forty hours. These and similar facts Borsche considers "ein experimenteller Beweis für die Kekulé'sche Benzolformel" \* and that the two chlorine atoms in (VIII) are not related to the rest of the molecule in the same way. As we had reason to doubt the validity of Borsche's deductions, our experiments were continued in the hope of preparing (IX) by a convenient method, and it has been shown that all the chlorine is replaced when (VIII) is boiled with ethyl sodioacetoacetate in benzene for twelve hours, and that therefore (VIII) is a useful starting substance in the preparation of tricyclic systems containing two heteroatomic nuclei linearly fused into each side of a central benzene nucleus.

Since the paper by Borsche and Bahr seems to have prevented the development of a valuable method of synthesis, it will be useful to indicate where their deductions are apt to be misleading. Their experimental method of comparing the activity of the chlorine atom in (XIV) with that of either chlorine atom in (VIII) leaves much to be desired. No care is taken to ensure the complete solution of the reacting substances in the ether used; and (XIV) will largely exist during the reaction in the form of the sodium derivative (XIV and ethyl acetoacetate and the final product will compete for the remaining sodium initially present in the ethyl sodioacetoacetate), which is less soluble in ether than (VIII). Hence the relative amounts of chlorine displaced under such conditions are at best only a very rough criterion of the activity of the chlorine atoms in each compound. But, assuming that the experimental conditions used admit of a just comparison, the theoretical conclusions (Borsche and Bahr, *loc. cit.*, p. 83) are scarcely justifiable. Any reluctance which (XIV) shows towards the introduction of another ethyl acetoacetate grouping into the molecule is not to be ascribed to a deep-seated structural difference between (VIII) and (XIV) (or to a difference in the molecular arrangement of the two chlorine atoms in VIII), so much as to a tendency, fairly general among organic compounds, to resist the intro-

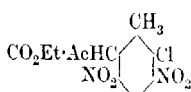
\* Kenner (T., 1914, 105, 2721, footnote) has already, however, from other points of view, cast doubt on Borsche's "experimental proof" of Kekulé's formula for benzene.

duction of many groups, especially when these are of the same type. The increasing difficulty encountered in the progressive nitration of many aromatic hydrocarbons, or in the progressive  $\alpha$ -chlorination of toluene or the toluoyl chlorides (this vol., p. 2212), are illustrative of this tendency. Perhaps phenomena of this kind, especially in the absence of strong polar effects, are really due to the damping effect on the recurrence of the reactive phase of the molecule, which often accompanies increase in molecular weight and volume. This "damping effect" is very well seen in the aliphatic series; to take two out of many examples in the literature, the stability towards hydrolysis by sodium hydroxide shown by the alkyl acyl-anilides increases with the normal introduction of methylene groups into the acidic group (Davis, T., 1909, 95, 1397), and the rate of hydration of aliphatic acid anhydrides (Sidgwick and Wilsdon, T., 1913, 103, 1959) is also lessened by lengthening the chain. From a consideration of this tendency (whatever the explanation in each case may be) it is to be expected\* that the chlorine atom in (XIV) would be somewhat less reactive than either of the chlorine atoms in (VIII), and consequently the deductions made by Borsche and Bahr concerning the structure of the benzene nucleus are unwarranted.

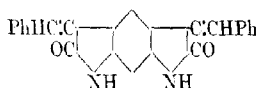
In this connexion, it is of interest to note that, whilst 2:6-dichloro-3:5-dinitrotoluene (XV) reacts with great ease to form *ethyl 5-chloro-2:4-dinitro-6-methylphenylacetoacetate* (XVI), the chlorine atom in the latter substance is far harder to replace than the chlorine atom in (XIV). The difference in this case is probably partly due to the great spatial congestion of groups in (XVI).



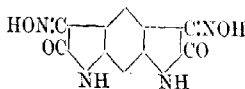
(XV.)



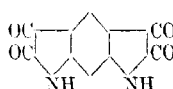
(XVI.)



(XVII.)



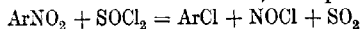
(XVIII.)



(XIX.)

\* The presence of the ethyl acetoacetate grouping in (XIV) no doubt enhances the negative polarity and the activity of the chlorine atom (compare Lapworth, *Mem. Manchester Phil. Soc.*, 1920, 64, ii, 1); but, for purposes of comparison, this is roughly balanced by the slight mutual activation of both chlorine atoms in (VIII), and consequently the "damping effect" referred to above is still to be expected. (For experimental proof of the mutual activating effect of meta-standing chlorine atoms, see Holleman and van der Hoeven, *Rec. trav. chim.*, 1920, 39, 736.)

The chief difficulty arising in the use of 1 : 3-dichloro-4 : 6-dinitrobenzene as starting material lies in the preliminary preparation of *m*-dichlorobenzene. For our first experiments *m*-chloronitrobenzene was reduced with iron filings and hydrochloric acid, and the *m*-chloroaniline produced converted into *m*-dichlorobenzene by the Sandmeyer reaction, but the overall yield was not good. A great improvement was effected by the use of a patented method (D.R.-P. 280739) for replacing aromatic nitro-groups by chlorine. *m*-Chloronitrobenzene was heated with thionyl chloride under pressure, when an excellent yield of *m*-dichlorobenzene was produced. *m*-Dinitrobenzene could doubtless be converted into *m*-dichlorobenzene in the same way, but the pressure produced is too great for the experiment to be conveniently carried out with the aid of glass tubes. The course of the reaction between thionyl chloride and aromatic nitro-derivatives is not clear; the equation



does not represent all the truth, for more than one molecule of thionyl chloride per nitroxy is required to bring the reaction to completion. This reaction is well worth further investigation.

In the condensation of 1 : 3-dichloro-4 : 6-dinitrobenzene with ethyl sodioacetoacetate (of which the quantities employed by Borsche and Bahr—twice the theoretical—were used), along with ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate (IX) some ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate was unexpectedly obtained. The constitution of this substance, which Borsche and Bahr (*loc. cit.*, p. 100) had already obtained from the condensation product of 1 : 3-dichloro-4 : 6-dinitrobenzene and ethyl sodiomalonate (reaction during seventy-five to one hundred hours being necessary for this condensation in ether), was proved by its conversion into the indefinitely melting 4 : 6-dinitrophenylene-1 : 3-diacetic acid (XI), and thence, by the elimination of carbon dioxide, into 4 : 6-dinitro-*m*-xylene. Small-scale experiments showed that the prolongation of the time of condensation, and the presence of alcohol during the condensation, both favoured the production of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate, and that this ester is also obtained by heating (IX) with a benzene solution of ethyl sodioacetoacetate. The alcohol necessary for the transformation of (IX) into ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate may be formed during the experiment by the decomposition of ethyl acetoacetate into dehydracetic acid or other cyclic substances, or perhaps by the decomposition of (IX) into compounds analogous to dehydracetic acid. No pure substance in support of this supposition has been isolated, but considerable quantities of an amorphous powder containing nitrogen and free from chlorine were formed. This

substance, which is soluble in alkali and in some organic solvents, might also be formed by the condensation of two molecules of (IX) with one molecule of (VIII).

Under the most favourable conditions, the total yield of (IX) and ethyl 4:6-dinitrophenylene-1:3-diacetate accounts for about 70 per cent. of the dichlorodinitrobenzene used. When the condensation in boiling benzene has been in progress for four hours or less, a considerable quantity of ethyl 5-chloro-2:4-dinitrophenyl-acetoacetate (XIV) can be detected.

Another matter of interest arising in the condensation of (VIII) with excess of ethyl sodioacetoacetate is the isolation of a small amount of long, asbestos-like needles melting at 169°. The substance is undoubtedly identical with that (m. p. 169°) Perkin and Thorpe (T., 1897, 71, 1194) obtained in very small amount in the condensation of ethyl  $\alpha$ -bromoisobutyrate with ethyl acetoacetate in the presence of zinc. They had insufficient of the substance for exhaustive analysis, but assigned to it the empirical formula  $C_{10}H_{10}O_4$ . Now, Collie and Chrystall (T., 1907, 91, 1802), by heating ethyl acetoacetate with its sodium derivative in alcohol, obtained needles melting at 168–169°, which, like the substance isolated in the course of the present investigation, gave striking colour changes with weak alkaline solutions. The substance obtained by Collie and Chrystall is a benzopyrone derivative and has the empirical formula  $C_{16}H_{16}O_6$ , for which the carbon and hydrogen content is very close (the difference being 1.4 and 0.1 per cent., respectively) to that required for the formula  $C_{10}H_{10}O_4$ . For the sake of comparison, we prepared some of the substance described by Collie and Chrystall, and found it, by means of a mixed-melting point determination, to be identical with our own. Our analysis confirmed the formula  $C_{16}H_{16}O_6$ , and hence there can be little doubt that the substance  $C_{10}H_{10}O_4$  described by Perkin and Thorpe is really the substance  $C_{16}H_{16}O_6$  investigated by Collie and Chrystall.

2:6-Dihydroxy-*m*- $\alpha$ -benzobispyrrole (XI), prepared from the ammonium salt of (XI) by reduction with ferrous sulphate and ammonia, and subsequent acidification, consists of needles and resembles its structural analogue, oxindole, in many chemical properties, but has a very high temperature of decomposition (over 300°), and is sparingly soluble in most organic solvents. It can, however, be sublimed in a vacuum, and resembles oxindole in its amphoteric nature and in the ease with which it reduces ammoniacal silver nitrate solution. Some of the hydrogen atoms are very reactive, for apart from the formation of two sodium salts, (XII) reacts with benzaldehyde to produce 2:6-diketo-3:5-dibenzylidene-2:3:5:6-tetrahydro-*m*- $\alpha$ -benzobispyrrole (XVII). This

is a coloured substance like benzylideneoxindole (Wahl and Bagard, *Bull. Soc. Chim.*, 1909, [iv], 5, 1033), but has a much higher melting point and is only sparingly soluble in organic solvents.

Attempts were made to prepare 3 : 5-dioximino-2 : 6-diketo-2 : 3 : 5 : 6-tetrahydro-*m*- $\alpha$ -benzbispyrrole (XVIII) and thence 2 : 3 : 5 : 6-tetraketo-2 : 3 : 5 : 6-tetrahydro-*m*- $\alpha$ -benzbispyrrole (XIX)—the analogue of isatin—but our experiments did not result in the formation of pure substances. However, the crude tetraketo-compound is analogous to isatin in many respects, giving, for example, an intense coloration when condensed with thiophen (see p. 2654).

To summarise, the *m*- $\alpha$ -benzbispyrrole derivatives so far obtained resemble their indole analogues very closely in chemical properties, but are far less soluble in neutral solvents and melt or decompose at considerably higher temperatures.

#### EXPERIMENTAL.

##### *Condensation of Ethyl Oxalate with Dinitromesitylene.*

The condensation of dinitromesitylene with ethyl oxalate in the presence of sodium ethoxide requires careful temperature control. An alcoholic solution of these substances remains perfectly colourless when kept for three weeks at room temperature, but, on the other hand, when the solution is boiled for two hours a reaction takes place and the product consists of a viscous, black tar. At 40°, however, a yellow coloration is produced which gradually becomes red. The condensation is accordingly carried out as follows: To a solution of sodium (3.1 grams = 4 atoms) in absolute alcohol (150 c.c.), ethyl oxalate (11 grams = slight excess over 2 mols.), and dinitromesitylene (7 grams = 1 mol.) are added. The mixture is warmed to 40° with shaking, when the dinitromesitylene dissolves and is kept under anhydrous conditions with occasional agitation at 40–45° for three days. The dark-coloured reaction product is decomposed with concentrated hydrochloric acid (15 c.c.), most of the alcohol removed by distillation, the residual product poured into water, rendered alkaline, the deep red solution filtered, and the filtrate extracted with ether. The clear solution is acidified and the brown precipitate collected after some time. The dry product, which weighs 5.2 grams and melts at 145–155°, is practically insoluble in water, for the acid mother-liquor, when exhaustively extracted with ether, yields less than 0.1 gram. The product is purified by repeated crystallisation from xylene.

*Dinitro-m-xylylpyruvic acid* (VI or VII) is sparingly soluble in most organic solvents, slightly soluble in boiling xylene, and dissolves in sodium hydroxide solution with the production of a deep

red solution. It crystallises from xylene in deep yellow plates melting with decomposition at 174–177° (Found: N = 9.9.  $C_{11}H_{10}O_7N_2$  requires N = 9.9 per cent.).

The condensation of dinitromesitylene at 40–45° with a large excess of ethyl oxalate and sodium ethoxide results in the same dinitro-*m*-xylylpyruvic acid. The latter substance is also formed at higher temperatures together with considerable quantities of tarry material.

The interaction of 4:6-dinitro-*m*-xylene, ethyl oxalate, and sodium ethoxide is equally unsatisfactory from the point of view of the present investigation. Since 4:6-dinitro-*m*-xylene is readily attacked by sodium ethoxide, the condensation can be conveniently carried out by adding at intervals, over the course of twelve hours, the calculated quantity of sodium ethoxide in alcohol to an alcoholic solution of dinitro-*m*-xylene and ethyl oxalate at room temperature. A reaction takes place at once; after a further thirty-six hours, the product is worked up in the way described in the dinitromesitylene experiment. In this way, some tar is formed, and also a light brown substance, slightly soluble in boiling xylene and in boiling ether, is obtained in about 30 per cent. yield. It dissolves with a blood-red coloration in sodium hydroxide solution and is fairly soluble in pure boiling acetone. This substance consists of microscopic crystals, sinters at about 250°, but is not completely fused below 300°. It suddenly deflagrates when cautiously heated in a flame (Found: N = 10.5.  $C_{10}H_8O_7N_2$  requires N = 10.4 per cent.). The nitrogen content of this compound probably indicates that it is fairly pure 2:4-dinitro-5-methylphenylpyruvic acid, but as it is evidently practically free from the desired dinitrophenylenedipyrvic acid, the substance was not further examined. It is hoped that the use of alcohol-free solvents will cause the reaction to take the desired direction.

*Ethyl 5-Chloro-2:4-dinitro-6-methylphenylacetoacetate (XVI).*

This substance is conveniently prepared by boiling for an hour an alcoholic solution of ethyl sodioacetoacetate (prepared from 7.5 grams of absolute alcohol, 8 grams of ethyl acetoacetate, and 1.4 grams of sodium) and 12.5 grams of 2:6-dichloro-3:5-dinitrotoluene (obtained as described, T., 1921, 119, 873). The deep red solution is poured into water and the oil produced dissolved in excess of dilute sodium hydroxide solution, and the filtered solution acidified with hydrochloric acid and then extracted with ether. The ethereal solution is dried over sodium sulphate, the ether removed, and the residual oil (which solidifies on standing) crystallised from alcohol, when 12 grams of (XVI) are obtained.

*Ethyl 5-chloro-2:4-dinitro-6-methylphenylacetoacetate* consists of stout, yellow crystals melting at 92–93° (Found: C = 45.6; H = 4.1.  $C_{13}H_{13}O_7N_2Cl$  requires C = 45.3; H = 3.8 per cent.). It is readily soluble in alkaline solutions (with the production of a red coloration) and in boiling alcohol, and is slightly soluble in cold alcohol or light petroleum. It is not easy to replace the chlorine atom by another ethyl acetoacetate group; when boiled for sixteen hours with excess of an alcoholic solution of ethyl sodioacetoacetate, two-thirds of (XVI) is recovered unchanged and only a small quantity of an oily substance can be isolated. A similar result is obtained with boiling benzene as solvent, and when the condensation is carried out in boiling xylene, extensive decomposition takes place. Attempts to prepare derivatives of 4-methyl-*m*- $\alpha$ -benzobispyrrole by this method were accordingly abandoned.

#### 1:3-Dichloro-4:6-dinitrobenzene (VIII).

The *m*-chloronitrobenzene required is obtained by the monochlorination of nitrobenzene after Varnholt (*J. pr. Chem.*, 1887, [ii], 36, 25), with ferric chloride as the catalyst; antimony trichloride is equally satisfactory. Chlorination takes place rapidly at 75–85°, and when a small proportion (5 per cent. or less) of catalyst is used the product can be straightway distilled. The distillate (b. p. 215–236°) is freed from unchanged nitrobenzene by combined fractionation and freezing out, and finally 180 grams of *m*-chloronitrobenzene, melting at 43–44°, are obtained from 265 grams of nitrobenzene.

*m*-Chloronitrobenzene (30 grams) is heated with thionyl chloride (50 grams) in a sealed tube at 190–200° for twelve hours.\* The product is carefully poured into water, made alkaline, and distilled in a current of steam. The colourless, heavy oil in the distillate is separated—the last portion with the aid of a little chloroform—dried over calcium chloride, and distilled, when 20 grams of *m*-dichlorobenzene, boiling at 170–180°, are obtained. This fraction is practically pure *m*-dichlorobenzene and is suitable for nitration without further purification.

1:3-Dichloro-4:6-dinitrobenzene is prepared in one operation

\* A very convenient substitute for small enamel-lined autoclaves for high-pressure work consists of bomb tubes of extremely hard, thick glass tubing about 50 cm. long and 3 cm. wide (external measurement). To the open end is sealed a piece of glass tubing about 12 cm. long and narrow enough to be worked in the ordinary blowpipe flame. Each tube has a capacity of about 200 c.c. and can be used several times without sealing on a new piece of narrow tubing. Those used in this research were obtained from C. Desaga, Hauptstrasse, Heidelberg.

by the nitration of *m*-dichlorobenzene after the method of Nietzki and Schedler (*Ber.*, 1897, **30**, 1666). We found it advantageous to use nitric acid of density 1.5 instead of 1.48. In this way, 30 grams of *m*-dichlorobenzene are converted into 32 grams of 1 : 3-dichloro-4 : 6-dinitrobenzene, m. p. 103°, and about 7 grams of a mixture of nitro-derivatives of *m*-dichlorobenzene.

*Condensation of Ethyl Sodioacetoacetate with 1 : 3-Dichloro-4 : 6-dinitrobenzene.*

When boiling xylene is used as solvent, the products formed rapidly decompose with the formation of dense, white fumes, but the condensation takes place smoothly when carried out in the following way. Ethyl acetoacetate (52 grams) is carefully added to molecular sodium (9.2 grams) covered with benzene (150 c.c.), and after the reaction has subsided the hot solution and suspension of ethyl sodioacetoacetate is treated with a solution of 1 : 3-dichloro-4 : 6-dinitrobenzene (24 grams) in benzene (50 c.c.). A vigorous reaction immediately takes place, the deep red solution is boiled for twelve hours on the water-bath, most of the benzene distilled off, and the residue treated with water (300 c.c.) and a small amount of sodium hydroxide solution. The benzene solution is filtered and dried, and evaporation yields a crystalline substance (*A*) weighing, in different experiments, from 4 to 6 grams. The red aqueous solution is extracted with ether, the ethereal solution (which contains a small amount of tar and of *A*) discarded, and the aqueous solution acidified with hydrochloric acid. An oil is produced which is repeatedly extracted with ether, the ethereal solution washed with water, dried over sodium sulphate, and the ether removed. The oily residue, which is free from chlorine, is dissolved in hot alcohol (100 c.c.) and crystals of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate (about 22 grams) separate on cooling and long standing. The mother-liquor on evaporation gives a tarry residue, of which part is only slightly soluble in ether. This least soluble portion is a light brown, amorphous powder containing nitrogen and readily soluble in alcohol, acetone, or ethyl acetate. This powder, which is formed in considerable quantity when the condensation is allowed to proceed for days, is difficult to obtain in a pure state. It probably contains some decomposition products of (IX) of the type indicated on page 2644.

Ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate separates from a mixture of carbon tetrachloride and light petroleum in coarse, bright yellow crystals melting at 108.5°. It is identified through its conversion by hydrolysis with acid into 4 : 6-dinitro-1 : 3-di-acetonylbenzene (XIII), very faintly yellow needles melting at



123° (Borsche and Bahr, *loc. cit.*, record 106—107° and 122—123°, respectively).

The crystalline substance (*A*) (practically insoluble in cold dilute alkali) formed during the condensation is not easily obtained perfectly pure. It crystallises from a mixture of chloroform and light petroleum in long, white needles softening at 80° and melting at 84° (Found: C = 48.9; H = 5.0.  $C_{14}H_{16}O_8N_2$  requires C = 49.4; H = 4.7 per cent.). It dissolves in hot sodium hydroxide solution with a red coloration, which rapidly becomes deep green and finally pale orange. When boiled for half an hour with 30 per cent. sulphuric acid, it is converted into an acid crystallising from water in pale yellow needles (Found: in anhydrous material, N = 10.1.  $C_{10}H_8O_8N_2$  requires N = 9.9 per cent.). The acid dissolves in excess of sodium hydroxide solution with an intense green coloration which rapidly becomes red. The melting point of the acid varies considerably with the rate of heating. It melts with decomposition at about 195° when rapidly heated, and at about 170° when slowly heated. It is converted in the course of a few minutes at 170° into carbon dioxide and a nitrohydrocarbon melting at 93°, which is 4 : 6-dinitro-*m*-xylene. The acid is finally shown to be 4 : 6-dinitrophenylene-1 : 3-diacetic acid (XI) (Borsche and Bahr, *loc. cit.*, p. 101, give m. p. 185—186° with evolution of carbon dioxide) by its conversion into the methyl ester, which agrees in melting point (95—96°) with methyl 4 : 6-dinitrophenylene-1 : 3-diacetate (Borsche and Bahr, *loc. cit.*). Hence the crystalline ester (*A*) formed in the condensation of ethyl sodioacetoacetate and 4 : 6-dinitro-*m*-dichlorobenzene is ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate, which melts (Borsche and Bahr, *loc. cit.*) at 82—83°.

The following experiments throw some light on the unexpected formation of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate in the condensation of (VIII) with ethyl sodioacetoacetate :

(1) The condensation was carried out in boiling benzene solution for a period of four days, when a larger amount of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate and a smaller amount of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate were formed than when the condensation required twelve hours.

(2) The condensation was carried out as before, but for a period of twenty-four hours and with the addition of two molecular proportions of alcohol. The yield of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate was still further increased, and that of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate very small.

(3) Ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate (1 gram; 1 mol.) was boiled for twenty-four hours in benzene with ethyl sodioacetoacetate (0.5 mol.). Half a gram of the original ester

was recovered unchanged and 0.3 gram of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetate was obtained.

These results are discussed in the theoretical portion of the paper.

From the condensation of ethyl sodioacetoacetate and 1 : 3-dichloro-4 : 6-dinitrobenzene still another crystalline substance was isolated. The ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate contained a minute amount of long, white needles, which were easily obtained pure, owing to their comparatively slight solubility in alcohol. The yield of this substance is increased to about 0.2 gram when a little free ethyl acetoacetate is added to the quantities condensed described on page 2649. The needles melt at 169° and are free from nitrogen and chlorine. The alcoholic solution, when mixed with ferric chloride solution (of which only a trace must be used), gives a deep violet colour. These and other properties agree with those of the substance melting at 169° obtained by Perkin and Thorpe (*loc. cit.*). We prepared the benzopyrone derivative described by Collie and Chrystall (*loc. cit.*) and found it to melt at 169°, alone or when mixed with the needles already isolated. The compound formed by heating ethyl acetoacetate and ethyl sodioacetoacetate was also analysed (Found : C = 63.25; H = 5.4.  $C_{18}H_{16}O_6$  requires C = 63.2; H = 5.2 per cent.) and the empirical formula of Collie and Chrystall confirmed.

#### 4 : 6-Dinitrophenylene-1 : 3-diacetic Acid.

A large proportion of the acid required was obtained from the ethyl ester formed as a by-product in the preparation of ethyl 4 : 6-dinitrophenylene-1 : 3-diacetoacetate. The ester is conveniently hydrolysed by boiling with excess of concentrated hydrochloric acid and an equal volume of alcohol (90 per cent.). By this means the ester is brought into solution and after boiling for ten minutes most of the alcohol is distilled off and the remaining solution concentrated, when the dinitrophenylenediacetic acid, which is fairly soluble in cold water, separates out in almost quantitative yield.

Part of the dinitrophenylenediacetic acid required was obtained by the hydrolysis and action of heat on ethyl 4 : 6-dinitrophenylene-1 : 3-dimalonate (X), first obtained by Borsche and Bahr (*loc. cit.*). It is more convenient not to use ether as solvent, but to carry out the condensation (with a small excess of ethyl sodiomalonate) in boiling benzene for a period of twelve hours. After removal of the benzene by distillation in a vacuum the crude residual ethyl dinitrophenylenedimalonate (1 part) is treated with glacial acetic acid (1 part) and water ( $\frac{1}{2}$  part), and concentrated sulphuric acid ( $\frac{1}{2}$  part) is gradually added to the mixture, heated on the water-bath.

When the evolution of carbon dioxide slackens, a further quantity ( $\frac{1}{2}$  part) of water is added and the mixture boiled for an hour. After cooling, the reaction product is extracted with ether, the ether removed, and the acetic acid may be eliminated from the residual liquid mixture of acetic and dinitrophenylenediacetic acids by evaporation over alkali, as recommended by Borsche. The separation can, however, be expedited by taking advantage of the slight solubility of lead 4:6-dinitrophenylene-1:3-diacetate in cold water. It is noteworthy that this salt is soluble in an excess of alkali acetate and in acetic acid. In this way, 1:3-dichloro-4:6-dinitrobenzene is converted into 4:6-dinitrophenylene-1:3-diacetic acid in a yield of 60 per cent.

*2:6-Dihydroxy-m- $\alpha$ -benzobispyrrole (XII).*

A hot solution of ferrous sulphate (80 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) in water (150 c.c.) is gradually added with stirring to a solution formed by dissolving 4:6-dinitrophenylene-1:3-diacetic acid (5.7 grams) in a mixture of equal volumes of ammonia (30 c.c.;  $d$  0.880) and water. Reduction rapidly takes place, the product is heated on the water-bath, filtered hot, and the precipitate well washed with boiling water. The iron-free filtrate is concentrated on the water-bath, diluted with water, and again concentrated, and this procedure repeated until the liquid no longer smells of ammonia and has a volume of about 80 c.c. The liquid, from which some of the desired substance has already separated, is treated with 20 c.c. of *N*-sulphuric acid and left over-night. The brown substance which separates is dissolved in hot *N*-sodium hydroxide solution (30 c.c.), and the hot filtered solution treated with hot *N*-sulphuric acid solution (30 c.c.), when crystals of 2:6-dihydroxy-m- $\alpha$ -benzobispyrrole rapidly separate and after twelve hours a yield of 2.7 grams is obtained. It is, however, not pure (Found:  $\text{C} = 62.3$ ;  $\text{H} = 4.4$ .  $\text{C}_{14}\text{H}_8\text{O}_2\text{N}_2$  requires  $\text{C} = 63.8$ ;  $\text{H} = 4.3$  per cent.) and is purified by repeated crystallisation from water or methyl alcohol, when very light brown needles are obtained, or by sublimation in a vacuum, when it is isolated in a perfectly colourless condition. However, the crude product, in which the chief impurity is a small amount of non-volatile substance insoluble in mineral acid, can be sufficiently purified for many purposes by dissolving it in a little warm concentrated hydrochloric acid and diluting the filtered solution with water, when the dihydroxybenzobispyrrole is reprecipitated.

2:6-Dihydroxy-m- $\alpha$ -benzobispyrrole consists of colourless, silky needles which begin to sinter at about  $300^\circ$  and partly melt and completely decompose between  $300^\circ$  and  $350^\circ$ . The temperature of decomposition varies considerably with the rate of heating

(Found: C = 64.1; H = 4.5; N = 14.7.  $C_{10}H_8O_2N_2$  requires C = 63.8; H = 4.3; N = 14.9 per cent.). When carefully heated, it sublimes at 30 mm. with some decomposition. It dissolves readily in dilute sodium hydroxide solution and is not reprecipitated by carbon dioxide. It is a very weak base (this fact and its sparing solubility in neutral organic solvents rendered the preparation of the pure hydrochloride impossible), but dissolves in excess of cold concentrated hydrochloric acid, and is more soluble in cold dilute aqueous mineral acid, sodium carbonate, and ammonia solutions than in cold water. It is rather soluble in boiling water, less soluble in boiling methyl alcohol, and slightly soluble in the cold solvents. It is practically insoluble in boiling ether, acetone, chloroform, benzene, xylene, or benzaldehyde. The aqueous solution gives no coloration with ferric chloride and reduces ammoniacal silver nitrate and potassium permanganate solutions even in the cold. When a sodium hydroxide solution of 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole is treated with benzenediazonium chloride, a brownish-red precipitate insoluble in a large excess of sodium hydroxide solution is at once formed, but this derivative is difficult to obtain in a pure state.

The *monosodium* salt of 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole is formed by adding the latter substance with stirring to a small quantity of 2*N*-sodium hydroxide at the ordinary temperature until no more dissolves. The excess of dihydroxybenzbispyrrole is at once filtered off and the filtrate, from which the air is now excluded, rapidly deposits the monosodium salt in very light brown prisms containing a large amount of water of crystallisation, of which the last traces are only very slowly lost at 150° (Found: in anhydrous substance, \*C = 56.45; H = 3.7; Na = 10.9.  $C_{10}H_7O_2N_2Na$  requires C = 57.1; H = 3.3; Na = 10.95 per cent.). When the salt is boiled with water and the solution cooled, some dihydroxybenzbispyrrole is precipitated in colourless needles.

What is presumably the *disodium* salt from 2:6-dihydroxybenzbispyrrole and a slight excess of cold concentrated caustic soda solution forms almost colourless needles extremely soluble in cold water. Owing to its great solubility, sufficient was not obtained for analysis. The aqueous solution does not deposit 2:6-dihydroxybenzbispyrrole when boiled and cooled. Aqueous solutions both of the mono- and di-sodium salts immediately give a scarlet coloration with phenolphthalein.

2:6-Diketo-3:5-dibenzylidene-2:3:5:6-tetrahydro-*m*- $\alpha$ -benzbispyrrole (XVII).—2:6-Dihydroxy-*m*- $\alpha$ -benzbispyrrole (0.3 gram) is

\* Allowance is made for the carbon retained as sodium carbonate in the boat.

boiled with benzaldehyde (2 c.c.), when no appreciable reaction occurs. A minute trace of piperidine is introduced into the hot suspension, which is again boiled, when a vigorous reaction takes place and a clear red solution is produced. After boiling for one minute, the solution is allowed to cool and orange crystals separate even above  $100^{\circ}$ . The crystals (0.4 gram) are collected and washed consecutively with ether, cold dilute sodium hydroxide solution, water, and then dried. The condensation can also be carried out in alcohol containing piperidine, after the method of preparing benzylideneoxindole (Wahl and Bagard, *loc. cit.*), but the reaction is slow. In both cases, the product consists of deep orange rhombohedra sintering at about  $300^{\circ}$  and melting with decomposition at  $315^{\circ}$  (Found: C = 78.7; H = 4.4; N = 7.4.  $C_{24}H_{16}O_2N_2$  requires C = 79.1; H = 4.4; N = 7.7 per cent.). It is sparingly soluble in organic solvents, but can be recrystallised from large quantities of ethyl acetate or ethyl alcohol. It is insoluble in cold dilute sodium hydroxide solution, but when boiled with concentrated sodium hydroxide solution a turbid brown coloration is formed which becomes a clear bright red on adding alcohol. Great dilution with alcohol produces a yellow solution. 2:6-Diketo-3:5-di-benzylidene-2:3:5:6-tetrahydro-*m*- $\alpha$ -benzbispyrrole dissolves in cold concentrated sulphuric acid to produce a clear, non-fluorescent, deep orange solution, from which an amorphous, yellow substance is precipitated on dilution with water.

2:6-Dihydroxy-*m*- $\alpha$ -benzbispyrrole and Nitrosating Agents.—The action of nitrous acid on a cold hydrochloric acid solution of 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole causes an immediate precipitation of a yellow powder insoluble in cold concentrated hydrochloric acid and soluble in cold sodium hydroxide solution with the formation of a clear brownish-red solution. This substance, however, is not pure, and the action of amyl nitrate (with hydrogen chloride or sodium ethoxide as condensing agents) on 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole likewise produces an impure oximino-derivative. Nitrosation, with rapid subsequent hydrolysis, by the gradual addition of dilute sulphuric acid to a boiling aqueous solution of 2:6-dihydroxy-*m*- $\alpha$ -benzbispyrrole and sodium nitrite, causes the formation of a red precipitate which, after continued hydrolysis with acid and purification by solution in cold alkali, is obtained on reprecipitation with acid as an amorphous, dark red precipitate. This crude 2:3:5:6-tetraketo-2:3:5:6-tetrahydro-*m*- $\alpha$ -benzbispyrrole (XIX) dissolves in cold alkali with an intense red coloration, is slightly soluble in boiling water, and practically insoluble in organic solvents, cold water, or cold concentrated hydrochloric acid. When warmed with a trace of thiophen (or commercial benzene) and concentrated sulphuric

acid, an intense deep green coloration is obtained. The analysis of this isatin analogue is, however, far from satisfactory, and the substance has not yet been prepared in a pure or crystalline condition. The high and rather indefinite melting points and the sparing solubility in organic solvents, as well as the dual character of the *m*- $\alpha$ -benzispyrrole derivatives, sometimes make their purification difficult.

The investigation of the properties of the parent substance, *m*- $\alpha$ -benzispyrrole, and of some further derivatives, and particularly their behaviour on continued oxidation, is contemplated.

The authors thank Professor W. H. Perkin, F.R.S., for directing their attention to this line of research, and for the kindly interest he has taken in the work throughout its course, and one of us (W.D.) also wishes to make due acknowledgment to the Ramsay Memorial Fund.

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### CCCXIX.—*The Molecular Scattering of Light in n-Pentane.*

By RAMAVENKATASUBBA VENKATESWARAN.

A NEW field of work which promises to prove of great importance in physical chemistry was opened up by the experimental researches of Smoluchowski (*Bull. Acad. Sci. Cracovie*, 1916, **31**, 218), Cabannes (*Compt. rend.*, 1915, **160**, 62; *Ann. Physique*, 1920, **15**, 1), and the present Lord Rayleigh (*Proc. Roy. Soc.*, 1918, **94**, 453) on the molecular scattering of light in gases and vapours, and especially by the discovery by Rayleigh that the light scattered by gases and vapours in a direction transverse to the primary beam is in general not completely polarised, indicating an optical anisotropy of the molecules. The measurements of Cabannes and of Rayleigh are in general agreement with the theory of molecular scattering of light developed by the late Lord Rayleigh, according to which  $\alpha$ , the fraction of the incident energy which is scattered in passing through unit volume of the substance, is given by the formula

$$\alpha = \frac{32\pi^3}{3} \frac{(n-1)^2}{N\lambda^4} \dots \dots \dots (1)$$

where  $N$  is the number of molecules per unit volume,  $n$  the refractive index of the medium, and  $\lambda$  the wave-length of the incident

light. The scattering of light in passage through dust-free liquids has also been observed by the present Lord Rayleigh (*Proc. Roy. Soc.*, 1918, **95**, 174) and Martin (*J. Physical Chem.*, 1920, **24**, 478; 1922, **26**, 75) and it was found that the scattering power of the liquid studied (ether) is considerably smaller than that given by formula (1), although, owing to the greater density of the liquid, the absolute magnitude of the effect is many times greater than in the vapour phase.

Of an entirely higher order of magnitude is the well-known phenomenon of strong opalescence exhibited by substances in the neighbourhood of the critical state. This phenomenon was qualitatively studied by Travers and Usher (*Proc. Roy. Soc.*, 1906, **78**, 247), S. Young (*ibid.*, p. 262), and F. B. Young (*Phil. Mag.*, 1910, [vi], **20**, 793), and quantitatively by Kammerlingh Onnes and Keesom (*Proc. Roy. Soc. Amsterdam*, 1908, **10**, 173). An explanation of the phenomenon on thermodynamic principles as due to accidental deviations of density was put forward by Smoluchowski (*Ann. Physik*, 1908, **25**, 205), and, later, Einstein (*ibid.*, 1910, **33**, 1275) obtained from Maxwell's equations of the electromagnetic field an expression for the intensity of the light scattered in consequence of such deviations. He showed that the fraction,  $\alpha$ , of the incident energy scattered in the substance per unit volume is

$$\alpha = \frac{8\pi^3}{27} RT^3 \frac{(n^2 - 1)^2 (n^2 + 2)^2}{N_1 \lambda^4} \dots (2)$$

where  $R$  is the gas constant,  $N_1$  the Avogadro number,  $\beta$  the isothermal compressibility of the substance,  $n$  the refractive index, and  $\lambda$  the wave-length of the incident light. Keesom (*ibid.*, 1911, **35**, 591) tested this formula over a range of  $2.35^\circ$  above the critical point of ethylene and found good agreement except in the immediate neighbourhood of the critical point.

The subject has gained a new significance as the result of the work of Raman ("Molecular Diffraction of Light," by C. V. Raman, published by the Calcutta University Press, 1922. See also *Nature*, 1921, **108**, 402; *Proc. Roy. Soc.*, 1922, **101**, 64), who has shown that the three phenomena mentioned above, namely, scattering of light by gases and vapours, scattering by liquids, and critical opalescence, which are of such different orders of magnitude and apparently so distinct, stand in reality in the closest relationship to each other, their magnitudes in each case being given by the Einstein-Smoluchowski formula (2), and further that this law, which reduces to Rayleigh's formula in the special case of a gas obeying Boyle's law, is much more generally applicable than (1), and should be regarded as the fundamental relation determining

the scattering power of fluid media. The theory of Einstein-Smoluchowski does not, however, take into consideration the influence of molecular ætropy, and has to be modified. The magnitude of this correction and its variations with temperature and pressure have been discussed by Raman and are referred to below. The subject bears very closely on various physicochemical conceptions such as the anisotropy of the molecule, molecular association, etc., and it is thus of importance to make a thorough investigation of the scattering of light in a large number of substances and to determine the validity of the theoretical results over the widest possible range of experimental conditions. A series of researches with this object in view has been undertaken at the suggestion of Prof. Raman. The cases of ether and benzene have been studied by Mr. K. R. Ramanathan, and the results will shortly be published. The present paper describes a similar study made with *n*-pentane both in the liquid and saturated vapour phases and in the gaseous phase above the critical temperature up to 214°.

#### EXPERIMENTAL.

The *n*-pentane used in these experiments had been fractionally distilled, the middle fraction, boiling at 37—38°, being then redistilled in a vacuum directly into the observation bulb, which was of 1 inch external diameter. The form of apparatus used was that employed by Martin to obtain dust-free liquids.

The glass bulb containing the required quantity of dust-free liquid was painted black except at three places, two at the sides for the admission and exit of light and the third, at the base, for the observation of the scattered light. The bulb was mounted at the centre of a stout iron cross-tube similar to the one employed by Lord Rayleigh. The contents of the bulb could be raised to any particular temperature and the temperature maintained constant within a few tenths of a degree for hours, the heating being conducted by passing an electric current through a coil of wire wound round the iron cross-tube. The cross-tube was mounted horizontally and a narrow cone of sunlight was focussed at the centre of the bulb by means of a lens. With this arrangement, the track of the light inside the bulb was easily visible through the window at the base of the bulb.

A quantity of pure redistilled benzene (dust-free) was placed in a rectangular glass bottle, and the track of light obtained by concentrating sunlight by a lens of the same focal length as the one mentioned above formed the standard for measuring the intensity of the scattered light in pentane. The image of the track of light

in benzene was brought into the same field of view as that of pentane by means of two totally reflecting prisms. The photometry was carried out with an Abney rotating sector disk. Different apertures of known diameter could be introduced in front of either lens in order to regulate the brightness and thus facilitate measurement; this has the additional advantage of minimising the heating effect of the cone of light.

The measurements thus obtained express the scattering power of pentane in the liquid or vapour phase as the case may be, in terms of the scattering power of liquid benzene at the temperature of the laboratory. It is desirable to express the scattering power in terms of that of liquid ether, as this forms a convenient standard. In order to effect this, a bulb containing dust-free ether at 35° was placed inside the cross-tube, the scattering power of the ether was compared with that of the benzene outside, and the values for pentane in terms of the benzene standard were multiplied by the ratio of the scattering power of benzene to that of ether, thus giving the scattering power of pentane in terms of that of liquid ether at 35°.

As the bulb containing ether was mounted in the same cross-tube, the substance studied (pentane) and the standard (ether) were in precisely the same conditions of experimentation. In the case of pentane vapour, however, a small correction is required for the loss of light on reflection at the interior walls of the bulb. This correction, which amounts to about 6 per cent., was applied to the observed values for the scattering power of pentane vapour.

#### *Results.*

The observed values for the scattering power of *n*-pentane, in the saturated vapour phase, in the gaseous phase, and in the liquid phase, are given in the second column of Tables I, II, and III, respectively, the intensity of the scattered light being expressed in terms of that in liquid ether at 35° as standard. In the third column are given the theoretical values indicated by the Einstein-Smoluchowski formula after applying the correction for the imperfect polarisation of the scattered light as explained in a later paragraph.

The theoretical value according to the Einstein-Smoluchowski formula is  $T\beta(n^2 - 1)^2(n^2 + 2)^2/T_1\beta_1(n_1^2 - 1)(n_1^2 + 2)^2$ , where  $\beta$  and  $n$  are the compressibility and refractive index, respectively, of *n*-pentane at the absolute temperature  $T$ , and  $\beta_1$  and  $n_1$  are the corresponding quantities for ether at  $T_1(273 + 35^\circ)$ . The values of  $h$  at different temperatures were obtained by applying Lorentz's refraction formula  $(n^2 - 1)/(n^2 + 2) = k\rho$  ( $\rho$  being the density of the substance); from the values of density of saturated vapour

and liquid pentane given by S. Young (T., 1897, **71**, 58),  $k = 0.3538$  for *n*-pentane.

The values of  $\beta$ , the compressibility of pentane at different temperatures, were determined by plotting the pressure-volume data given by Rose-Innes and Young (*Phil. Mag.*, 1899, [vi], **47**, 355) and drawing tangents to the different isothermals at the points of saturation. In the case of vapour of *n*-pentane between  $180^\circ$  and  $197.2^\circ$ , the critical temperature, the pressure-volume data have not been given by these authors, and the values of  $\beta \left( = -\frac{1}{v} \cdot \frac{dv}{dp} \right)$  at these temperatures were calculated from the values of  $dp/dT$  given by Rose-Innes and Young by the application of Dieterici's relation,

$$\frac{dp}{dT} - \frac{p}{T} - \frac{cR}{v} = \frac{cR}{p} \cdot \frac{dp}{dv} \quad (c = 1.707 \text{ for } n\text{-pentane}).$$

The values of  $\beta$  obtained in this way were plotted along with the values of  $\beta$  obtained from the pressure-volume data, a smooth curve was drawn through them, and the value of  $\beta$  for saturated pentane vapour at any temperature was read from the curve.

The values of  $\beta$  for liquid pentane were obtained from Landolt's tables up to  $100^\circ$  and from the pressure-volume data given by Rose-Innes and Young above  $130^\circ$ . In order to determine the values of  $\beta$  and  $n$  for *n*-pentane in the gaseous phase above the critical point, it is necessary to know the actual mass of pentane used and the volume of the bulb; these were separately determined at the end of the experiment.

The fourth column contains the ratio of the scattering power of *n*-pentane at  $t^\circ$  to that of the same at  $87^\circ$ . In the fifth column are given the ratios of the density of the substance at  $t^\circ$  to that at  $87^\circ$ .

The results obtained show a satisfactory agreement with those calculated from the Einstein-Smoluchowski formula. Indeed, a closer agreement cannot be expected, if it is remembered that experimental difficulties, such as slight fluctuations of temperature, a trace of dissolved air or traces of impurities such as benzene in the pentane, have a large influence on the scattering power. Moreover, the theoretical values are not very accurate, as there is a little uncertainty in determining the compressibility from the curves, especially at the points of saturation. There can, however, be no doubt as to the validity of the Einstein-Smoluchowski formula for the scattering power of *n*-pentane in all three phases, liquid, saturated vapour, and gas. If the Rayleigh formula held good, the values in the fourth and fifth columns in Tables I and III

TABLE I.

Scattering of light in the saturated vapour of *n*-pentane.

Tem- perature.	Scattering power of <i>n</i> -pentane vapour		Scattering power of <i>n</i> -pentane vapour at <i>t</i> °	Density of sat- urated vapour of <i>n</i> -pentane at <i>t</i> °
	Scattering power of liquid ether at 35°.		Scattering power of the same at 87°.	Density of the same at 87°.
	Observed.	Calculated.		
87°	0.235	0.242	1.00	1.00
125.2	0.73	0.71	3.11	2.33
137	1.20	1.13	5.11	3.00
145	1.95	1.59	8.30	3.58
149	2.10	1.85	9.14	3.87
154	2.42	2.37	10.3	4.25
155.4	2.66	2.44	11.3	4.38
167	3.90	4.07	16.6	5.75
172	5.88	5.58	25.0	6.46
183	13.4	11.3	57.0	8.42
187	17.8	16.8	75.7	9.58
189	22.1	19.1	94.0	10.1
190.5	23.3	23.2	99	10.7
193	30.8	31.7	131	12.0
196	70.8	69.5	301	15.3

TABLE II.

Scattering of light in gaseous pentane above the critical point.

Tem- perature.	Scattering power of pentane vapour		Ratio of scat- tering power of gaseous pentane at $t^\circ$ to that of the same at $36.5^\circ$ .	Ratio of density of gaseous pen- tane at $t^\circ$ to that of the same at $36.5^\circ$ .
	Scattering power of liquid ether at $35^\circ$ .			
	Observed.	Calculated.		
200°	48.5	(26.0)	206	11.2
203	30.8	24.3	131	11.2
210	20.8	18.5	90	11.2
214	15.2	15.7	65	11.2

TABLE III.

Scattering of light in liquid *n*-pentane.

Tem- perature.	Scattering power of pentane vapour		Ratio of scatter- ing power of liquid pentane at $t$ to that of the same at $36.5^\circ$ .	Ratio of the den- sity of liquid pentane at $t^\circ$ to that of the same at $36.5^\circ$ .
	Scattering power of liquid ether at $35^\circ$ .			
	Observed.	Calculated.		
$36.5^\circ$	1.61	1.92	1.00	1.00
86.6	2.81	2.96	1.764	0.922
103.8	3.40	3.23	2.112	0.877
117.0	4.25	3.72	2.64	0.839
128.0	5.36	4.28	3.33	0.814
138.0	6.37	5.34	3.96	0.789
148.6	8.18	6.5	5.08	0.759
156.8	9.10	8.75	5.65	0.732

should have agreed. Actually this is far from being the case, the scattering power of the vapour increasing at a much greater rate than that proportional to its density, as the temperature is raised. It is evident that the Rayleigh formula breaks down completely for all three phases and that the "principle of random phase" on which he founded his theory of molecular scattering of light is not valid except in the case of a perfect gas.

#### *Polarisation of the Scattered Light.*

It was shown by Rayleigh by a photographic method that the light scattered by dust-free gases and vapours in a direction at right angles to the incident beam is, in general, imperfectly polarised. In the case of pentane vapour he found the ratio of the weak component to the strong in the scattered light was 1.2 per cent., the result being, however, marked as doubtful owing to the formation of a cloud in the observation tube. In order to study the effect of temperature and pressure on the polarisation of the scattered light, the extent of the imperfection of polarisation at the various temperatures was determined by the present author in the following manner. A cone of sunlight or light from an arc lamp was focussed at the centre of the observation bulb containing the liquid or vapour of pentane, and the scattered light was viewed through a double-image prism and a Nicol. The double-image prism was adjusted so as to bring the two images, the strong and the weak components, into line, and the Nicol was then turned until the two images were of equal brightness. The Nicol was then rotated to another position at which the two images were of equal brightness. The angle through which the Nicol was turned between the two positions was read on the graduated disk. The ratio,  $r$ , of the weak component to the strong is equal to the square of the tangent of half the angle and is a measure of the imperfectness of polarisation.

#### *Polarisation of the scattered light in pentane.*

Liquid	Temperature	30°	80°	86°	122°	151°	159°	173°
	Imperfection of polarisation	7.2	7.2	6.7	5.2	1.7	1.5	1.5 per cent.
Vapour	Temperature	144°	167°	181°	197°			
	Imperfection of polarisation	2.5	2.0	1.5	1.5 per cent.			

It will be seen that the degree of imperfection of polarisation of the scattered light in pentane vapour is very small, but it shows a marked diminution as the critical temperature is approached; in the case of the liquid, on the other hand, the degree of imperfection is fairly considerable at low temperatures, remains constant up to moderately high temperatures, and then rapidly falls to a



small value, which is the same as in the case of the vapour. There is no change in the degree of imperfection on passing through the critical point.

The explanation of the remarkable difference in the state of polarisation of the light scattered in vapours and in liquids and of its changes with temperature and pressure has been discussed by Raman. His theory may be briefly outlined as follows. The light scattered by a fluid may be divided into two parts, (1) the scattering of the one part is due to thermal fluctuations of density, and is determined by the positions of the molecules, its magnitude being given by the Einstein-Smoluchowski formula, and (2) the scattering of the other arises from the anisotropy of the molecules, the magnitude of the effect being determined by their varying orientation. Part (1), when observed in a direction transverse to the primary beam, consists wholly of polarised light, and part (2) almost wholly of unpolarised light. When the substance is in the state of rarefied vapour, both the position and orientation of the molecules may be assumed to be absolutely at random, and its power of scattering light is, as indicated by the Rayleigh law, proportional to its density. But when the vapour is compressed to such an extent that its pressure-volume relation deviates from Boyle's law, or when the substance passes into the state of liquid, the positions of the molecules in space no longer form a random distribution, and the part of the scattered light which is due to fluctuations of density ceases to be proportional to the density. In liquids, in fact, this part of the scattering becomes much smaller relatively to the vapour than the value proportional to the greater density, as can be seen from a comparison of the figures in Tables I and III. The orientation of the molecules, on the other hand, does not depart very greatly from a random distribution, and the unpolarised part of the scattered light which arises from differences of the properties of the molecules in different directions increases nearly in proportion to the density. The ratio of the unpolarised to the polarised part of the scattering should therefore be considerably greater for the liquid than for the vapour at the ordinary temperature. This is what is actually observed, and the same considerations also explain why the polarisation of the scattered light both in the liquid and the saturated vapour phases improves *pari passu* with the increased intensity of scattering as the temperature is raised.

It is obvious from what has been said above that owing to admixture of unpolarised light arising from the anisotropy of the molecules, the scattering of light actually observed must be greater than that given by the Einstein-Smoluchowski theory. The magni-

tude of the correction factor is easily found. The quantity  $r$ , which is a measure of the imperfectness of polarisation, is

$$r = \frac{\text{Intensity of weak component}}{\text{Intensity of strong component}},$$

and the complete mathematical investigation shows that the total intensity of the scattered light in a direction transverse to the primary beam is increased in the ratio  $(6 + 6r)/(6 - 7r)$ . This correction has been introduced in the figures contained in the third column of tables I, II, and III.

The author proposes to continue the investigation of the scattering of light in a large number of carbon compounds and of the degree of imperfection of polarisation of the scattered light, with a view to find out the relation between these quantities and the structure of the molecule.

In conclusion, I have great pleasure in acknowledging my indebtedness to Prof. C. V. Raman, under whose inspiring guidance the work was carried out.

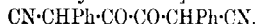
UNIVERSITY COLLEGE,  
RANGOON, BURMA.

[Received, July 3rd, 1922.]

### CCCXX.—Dyes derived from $\alpha\alpha'$ -Dicyanodibenzyl Diketone.

By SIKHIBHUSHAN DUTT and NIRMAL KUMAR SEN.

By the action of oxalic ester on benzyl cyanide in presence of alcoholic sodium ethoxide, Volhard (*Annalen*, 1894, **282**, 4) obtained a compound to which he gave the name diphenylketipic-dinitrile [ $\alpha\alpha'$ -dicyanodibenzyl diketone] and the constitution



He described it as crystallising in olive-green needles melting at  $272^\circ$ .

Employing his method, the authors obtained a substance which crystallised in glistening, bright yellow leaflets and melted at  $132^\circ$ . That this substance is  $\alpha\alpha'$ -dicyanodibenzyl diketone is indicated by the analytical data and also by the fact that, like other  $\alpha$ -diketones, it undergoes condensation with *o*-diamines to form azines. These condensation products, which are characterised by their crystallising power and dyeing properties, closely resemble the corresponding azines derived from benzil,  $\beta$ -naphthoquinone, and phenanthraquinone. Condensation has been effected with the following diamines: ethylenediamine, *o*-phenylenediamine,

2 : 3-tolylenediamine, 1 : 2-naphthylenediamine and its 5-sulphonic acid, 8-hydroxy-1 : 2-naphthylenediamine-6-sulphonic acid, 1 : 2 : 4-triaminobenzene, 2-aminodiphenylamine, 2-aminodi-*p*-tolylamine, phenyl-1-amino- $\beta$ -naphthylamine, 2-aminophenyl- $\alpha$ -naphthylamine, and 2-amino-4-anilinodiphenylamine.

Most of the condensation products are bright yellow substances which give the characteristic colour reactions of azines with concentrated sulphuric acid and dye wool in very uniform and fine shades from an acid bath.

#### EXPERIMENTAL.

*$\alpha\alpha'$ -Dicyanodibenzyl Diketone.*—2.5 Grams of sodium were dissolved in 40 c.c. of absolute alcohol, the solution was cooled, and a mixture of 7 grams of benzyl cyanide and 4.8 grams of ethyl oxalate in 40 c.c. of absolute alcohol added. The mixture was heated on the water-bath under reflux for half an hour and acidified with dilute hydrochloric acid. The yellow, crystalline precipitate, twice recrystallised from dilute acetic acid, formed brilliant, yellow, glistening leaflets, m. p.  $132^\circ$  (Found : N = 9.4.  $C_{18}H_{12}O_2N_4$  requires N = 9.72 per cent.).

The above process was subsequently modified by omitting the alcohol, the sodium being added directly to the mixture of benzyl cyanide and ethyl oxalate. The reaction, which was slow at first, proceeded with increasing vigour, and the whole mass became viscid. The product was acidified and the resulting precipitate crystallised as before.

#### Condensation with Diamines.

In the following preparations, unless otherwise stated, 2.8 grams of  $\alpha\alpha'$ -dicyanodibenzyl diketone were condensed, in glacial acetic acid, with the quantity of diamine recorded. In the formulae, X denotes CN-CHPh. The dyeing properties were tested on wool in an acid bath.

*$\alpha\alpha'$ -Dicyano-2 : 3-dibenzyl-5 : 6-dihydropyrazine,*  $\begin{matrix} X \cdot C \cdot N \cdot CH_2 \\ | \\ X \cdot C \cdot N \cdot CH_2 \end{matrix}$ , was prepared from 1.5 grams of ethylenediamine hydrochloride in about 30 c.c. of boiling water. The yellow colour of the diketone rapidly disappeared, and an almost colourless, crystalline substance was formed. This, recrystallised from dilute alcohol, was obtained in very pale yellow needles, m. p.  $155^\circ$  (Found : N = 18.4.  $C_{20}H_{16}N_4$  requires N = 18.0 per cent.).

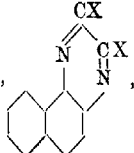
*$\alpha\alpha'$ -Dicyano-2 : 3-dibenzylquinoxaline,*  $C_6H_4 \begin{matrix} \swarrow N : CX \\ \searrow N : CX \end{matrix}$ , prepared from 1.2 grams of *o*-phenylenediamine, crystallised from 40 per cent.

DYES DERIVED FROM  $\alpha\alpha'$ -DICYANODIBENZYL DIKETONE. 2665

acetic acid in brilliant, yellow, glistening needles, m. p.  $227^{\circ}$  (Found: N = 16.2.  $C_{24}H_{16}N_4$  requires N = 15.6 per cent.). The substance dissolves in concentrated sulphuric acid with a blood-red colour, and dyes bright yellow shades.

$\alpha\alpha'$ -Dicyano-2 : 3-dibenzyl-8-methylquinoxaline,  $C_6H_3Me \begin{smallmatrix} \text{N:CX} \\ \text{N:CX} \end{smallmatrix}$ ,

prepared from 1.4 grams of 2 : 3-tolylenediamine, crystallised from dilute acetic acid in brilliant, orange-red needles, decomposing above  $250^{\circ}$  (Found: N = 14.8.  $C_{25}H_{18}N_4$  requires N = 14.9 per cent.). It dissolves in concentrated sulphuric acid with a violet colour, and dyes orange-red shades.

$\alpha\alpha'$ -Dicyano-2 : 3-dibenzyl-1 : 4-naphthaquinoxaline, 

prepared from 1.6 grams of 1 : 2-naphthylenediamine, crystallised from dilute acetic acid in bright orange-yellow needles, m. p.  $230^{\circ}$  (Found: N = 13.5.  $C_{26}H_{16}N_4$  requires N = 13.6 per cent.). It develops a violet colour with concentrated sulphuric acid, and dyes orange-yellow shades.

$\alpha\alpha'$ -Dicyano-7-amino-2 : 3-dibenzylquinoxaline,  $NH_2 \cdot C_6H_3 \begin{smallmatrix} \text{N:CX} \\ \text{N:CX} \end{smallmatrix}$ .

—5.6 Grams of the diketone and 4 grams of 1 : 2 : 4-triaminobenzene dihydrochloride were boiled together with 60 c.c. of water for half an hour. The dark violet solution obtained was filtered, rendered alkaline with sodium hydroxide, and the dark brown precipitate formed was crystallised from hot pyridine with the addition of dilute acetone, when the quinoxaline was obtained in yellowish-brown needles, which decomposed on heating (Found: N = 18.9.  $C_{24}H_{17}N_5$  requires N = 18.67 per cent.). It dissolves in concentrated sulphuric acid with a violet colour, and dyes violet shades.

$\alpha\alpha'$ -Dicyano-2 : 3-dibenzyl-1 : 4-naphthaquinoxaline-7-sulphonic acid,  $SO_3H \cdot C_{10}H_5 \begin{smallmatrix} \text{N:CX} \\ \text{N:CX} \end{smallmatrix}$ , was prepared by boiling the diketone

and 2.5 grams of 1 : 2-naphthylenediamine-5-sulphonic acid with 50 c.c. of water for about fifteen minutes. A clear solution was obtained which, on cooling, deposited the condensation product as a brownish-yellow mass. This was dissolved in sodium hydroxide, reprecipitated by hydrochloric acid, and finally crystallised from dilute acetic acid, glistening, yellow needles, decomposing above  $270^{\circ}$ , being formed (Found: S = 6.5.  $C_{28}H_{18}O_3N_4S$  requires S = 6.53 per cent.). The naphthaquinoxaline dissolves in con-

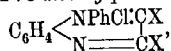
concentrated sulphuric acid with a violet colour, and dyes intense yellow shades.

$\alpha\alpha'$ -Dicyano-10-hydroxy-2:3-dibenzyl-1:4-naphthaquinoxaline.

8-sulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_4(\text{OH})\text{N}(\text{C}_6\text{H}_5)_2$  was prepared from 5.6

grams of the diketone and 5.4 grams of 8-hydroxy-1:2-naphthyl-enediamine-6-sulphonic acid as in the preceding case. The product, purified by dissolution in sodium hydroxide and precipitation from the filtered solution with hydrochloric acid, was a yellowish-brown, amorphous powder which decomposed on heating (Found: S = 6.6.  $\text{C}_{28}\text{H}_{18}\text{O}_4\text{N}_4\text{S}$  requires S = 6.32 per cent.). It dissolves in concentrated sulphuric acid with a reddish-violet colour and dyes chocolate shades on wool from a bath rendered alkaline with 2 per cent. sodium carbonate.

$\alpha\alpha'$ -Dicyano-1-phenyl-2:3-dibenzylquinoxalinium chloride,



was prepared from 2.2 grams of 2-aminodiphenylamine hydrochloride in 40 c.c. of hot glacial acetic acid and 4 c.c. of concentrated hydrochloric acid, the condensation product being deposited in fine, yellow needles, which decomposed on heating (Found: N = 11.6.  $\text{C}_{30}\text{H}_{21}\text{N}_4\text{Cl}$  requires N = 11.87 per cent.). The substance dissolves in concentrated sulphuric acid with an orange-yellow colour, and dyes bright yellow shades.

$\alpha\alpha'$ -Dicyano-1-phenyl-2:3-dibenzyl-1:4-naphthaquinoxalinium

chloride,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NPhCl}\cdot\text{CX} \\ \text{N}=\text{CX} \end{array}$ , similarly prepared from 2.4 grams of

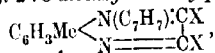
phenyl-1-amino- $\beta$ -naphthylamine, was, after two minutes' boiling and dilution with hot water, deposited in minute, orange-yellow needles, which decomposed on heating (Found: C = 77.6; H = 4.2.  $\text{C}_{34}\text{H}_{23}\text{N}_4\text{Cl}$  requires C = 78.1; H = 4.7 per cent.). It dissolves in concentrated sulphuric acid with an orange-red colour, and dyes orange shades.

$\alpha\alpha'$ -Dicyano-1- $\alpha$ -naphthyl-2:3-dibenzylquinoxalinium chloride,

$\text{C}_6\text{H}_4 \begin{array}{c} \text{NCl}(\text{C}_{10}\text{H}_7)\cdot\text{CX} \\ \text{N}=\text{CX} \end{array}$ , prepared from 2.4 grams of the diketone

and 1.2 grams of 2-aminophenyl- $\alpha$ -naphthylamine as above, crystallised from glacial acetic acid in red, microscopic needles (Found: C = 77.8; H = 4.6.  $\text{C}_{34}\text{H}_{23}\text{N}_4\text{Cl}$  requires C = 78.1; H = 4.4 per cent.). The substance dissolves in concentrated sulphuric acid with a reddish-violet colour, and dyes bright red shades.

$\alpha\alpha'$ -Dicyano-1-*p*-tolyl-2:3-dibenzyl-6-methylquinoxaline,



prepared by means of 2.5 grams of 2-aminodi-*p*-tolylamine hydro-

chloride, crystallised from acetic acid in shining, brown needles (Found: N = 11.7.  $C_{32}H_{25}N_4$  requires N = 12.04 per cent.). It dissolves in sulphuric acid with an orange-brown colour, and dyes brown shades.

*αα'*-Dicyano-6-anilino-1-phenyl-2:3-dibenzylquinoxalinium chloride,  $NHPh \cdot C_6H_5 \cdot \begin{matrix} NPhCl \cdot CX \\ N \equiv CX \end{matrix}$ , prepared from 1.4 grams of the diketone and 1.4 grams of 2-amino-4-anilinodiphenylamine in presence of glacial acetic and concentrated hydrochloric acids, crystallised from the solution in microscopic, bluish-green needles, which decomposed on heating (Found: C = 77.2; H = 4.2.  $C_{36}H_{26}N_6Cl$  requires C = 76.7; H = 4.6 per cent.). It dissolves in concentrated sulphuric acid with a green colour, and dyes fine bottle-green shades.

Further work in this direction is in progress.

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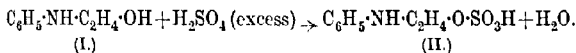
[Received, May 22nd, 1922.]

## CCCXXI. — *Esters of the Hydroxyalkylarylamines.*

### *Part I. Acid Sulphuric Esters of the Simple Monohydroxyethylarylamines.*

By KENNETH HERBERT SAUNDERS.

DURING a research in the latter part of 1920 on the preparation of the hydroxyethylarylamines, it was suggested by Prof. A. G. Green that the action of sulphuric acid on the alcoholic hydroxy-group in these compounds should lead to derivatives of ethyl hydrogen sulphate:



On experiment, it was found that if hydroxyethylaniline (I) is dissolved in two to three times its own weight of concentrated sulphuric acid at the temperature of the steam-bath, in a short time a test portion, on addition to excess of alkali, no longer gives oily drops of the original base, but dissolves to a clear solution. The conditions preclude any possibility of sulphonation; which, in the case of aniline, does not take place below 200° with ordinary sulphuric acid. The proof that the soluble compound so obtained is in fact a sulphuric ester (II) will be shown in the sequel.

Further study has shown that the reaction is a general one, all

hydroxyalkylarylamines which have been examined giving similar sulphuric esters. The reaction is capable of extensive application in dyestuff manufacture (see Brit. Pat. 181750 of 1922), but it is proposed to deal here only with the conditions of formation and chemical relationships of the simpler members of the group. Those compounds which contain two alcoholic hydroxy-groups present a rather more complex case which will be dealt with in a separate communication.

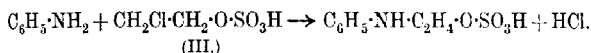
The action of sulphuric acid on various hydroxyethylarylamines has up to the present been supposed to lead to one of the three types of heterocyclic compounds represented by *N*-diphenylpiperazine, *N*-phenylmorpholine, and phenmorpholine. The latter two were first obtained by Knorr from dihydroxyethylaniline and mono-hydroxyethyl-*o*-aminophenol, respectively (*Ber.*, 1889, 22, 2081 *et seq.*), whilst Rindfuss and Harnack (*J. Amer. Chem. Soc.*, 1920, 42, 1720) have shown that sulphuric acid, among many other dehydrating agents, removes a molecule of water from two molecules of hydroxyethylaniline, thereby producing *N*-diphenylpiperazine. In all the above work, sulphuric acid has been considered purely in the rôle of dehydrating agent, and the formation of sulphuric esters does not seem to have been surmised. Knorr (D.R.-P. 95854) specifically claims 70 per cent. sulphuric acid as the most efficient for ring formation, but it has been found that long heating of dihydroxyethylaniline with monohydrate at 100° produces merely a trace of the morpholine. Hence, although there is an ever-present tendency for both secondary and tertiary hydroxyethylarylamines to lose water to form heterocyclic compounds, yet by the use of appropriate methods it is possible to produce an ester of any arylamine containing a hydroxyethyl group, whether the arylamine exists as such or is combined in a more complex form such as a dyestuff or intermediate. Even when ring closure occurs, it is extremely probable that it is preceded by sulphuric ester formation, and in this connexion Knorr's use of an extremely strong hydrolytic agent, 70 per cent. sulphuric acid, is significant.

All members of this new range of compounds may be named as derivatives of  $\beta$ -aminoethyl hydrogen sulphate, but as it is obvious that such a system of nomenclature would be difficult for complex dyestuffs, it has been proposed to refer to the alkylsulphuric acid group attached to nitrogen as the "sulphato" group, and the simplest member of the series, *N*-phenyl- $\beta$ -aminoethyl hydrogen sulphate (II), is thus termed "sulphatoethylaniline." Similarly, the dyestuffs which can be derived from such intermediates are referred to as the "sulphato" dyestuffs and the process of esterifying the hydroxy-group as "sulphation."

The process of sulphation can be carried out in several ways, and the choice of method depends on such considerations as the use to which the product is to be put.

The first and simplest method, as mentioned above, consists in dissolving the hydroxyethylarylamine in strong sulphuric acid in such excess that esterification proceeds virtually to completion. Under these conditions, all types of compounds do not yield sulphato-derivatives with equal ease, and the monohydroxyethylarylamines, such as hydroxyethylaniline, require heating at 100° with several molecules excess of acid to attain entire solubility in aqueous alkalis. By neutralising the diluted sulphuric acid solutions with alkali or by liming out, solutions of the sulphato-salts are obtained which are not convenient starting-points for the isolation of the pure esters, as the process is beset with the same difficulties found in the attempt to isolate ethyl hydrogen sulphate itself in high yield and purity. Such solutions can, however, well be used for producing more complex derivatives of the product such as indamines or nitroso-compounds, and are easily estimated by titration with standard solutions of suitable diazo-salts.

A second method of arriving at the sulphato-compounds consists in acting on arylamines with  $\beta$ -chloroethyl hydrogen sulphate (III). This latter substance is obtained from ethylene chlorohydrin and excess of sulphuric acid in exactly the same way as ethyl hydrogen sulphate is obtained from ethyl alcohol. In boiling neutral aqueous solution, it reacts with aniline, a carbonate being used to neutralise the hydrochloric acid produced.



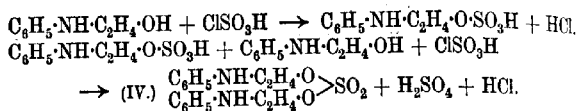
The solution obtained in this way is identical with that produced by acting on hydroxyethylaniline with excess of sulphuric acid. Partly on account of the necessity of employing dehydrated ethylene chlorohydrin, and also because the yields are indifferent, this method is not to be compared for convenience with the previous one.

The third method available for the production of the sulphato-compounds has the advantage that by its use the simpler substances such as ethylsulphatoaniline may be readily obtained in the solid state in good yield. Chlorosulphonic acid is used as the esterifying agent in this case, and may be applied to an hydroxyethylarylamine in theoretical proportions either alone, or, better, in solution or suspension in a neutral solvent such as tetrachloroethane, whereby the vigorous reaction is toned down and the sulphato-derivative obtained direct.

It is interesting to note that this reaction does not always yield



the sulphato-compound exclusively, as might be expected, but the amount obtained varies widely with different amines from the amount required by theory. The explanation appears to be that the chlorosulphonic acid plays the dual rôle of esterifying agent and dehydrator, producing the neutral ester (IV) in addition to the sulphato-compound, the amounts being proportional to the relative velocities of the two reactions.



It is intended to make a further study of this side reaction and its products in the near future.

When obtained in the pure state, the simple sulphato-compounds are found to be white solids which can be crystallised from suitable solvents, whilst some give sharp melting points at high temperatures without immediate decomposition. The monobasic acids of the type of sulphatoethylamine are sparingly soluble in cold water; their salts with the alkali metals dissolve very readily, those with the alkaline earths not quite so easily. Boiling ethyl alcohol dissolves them to some extent, and is the best medium for recrystallisation. The presence of the acid radicle in the side chain greatly reduces the basicity of the amino-nitrogen atom, so that salts with acids are only formed in strongly acid solution, and these decompose on dilution or drying. One result of this is that sulphatoethylaminobenzene, in contrast to methyl-orange, is useless as an indicator, since moderate dilution of the red acid solution changes the colour to yellow owing to hydrolysis of the red dye-acid complex.

Chemically, the sulphato-compounds show reactions characteristic of the units of their structure—arylamine and alkyl sulphate. A freshly prepared dilute solution of a sulphato-compound gives no precipitate with barium chloride. If concentrated, the more sparingly soluble barium salt may be precipitated, but redissolves on heating. That these substances are actually sulphuric esters is, however, shown by the fact that if the barium salt is boiled for long, particularly in concentrated solution, barium sulphate is thrown down. Like ethyl hydrogen sulphate, they are more rapidly hydrolysed by acids than by alkalis, the rate with the latter being very slow. Apparently, sulphato-compounds show greater stability in dilute than in concentrated solution, which is the cause of the difficulty encountered in crystallising them from water, since at the crystallising point hydrolysis occurs and the products contaminate the sulphato-compound. Long-continued, drastic treat-

ment is necessary to effect complete hydrolysis. In this respect, they differ most markedly from the members of another series of substances to which they bear a resemblance, namely, the aryl-aminomethane-*o*-sulphonic acids obtained by acting on arylamines with formaldehyde-bisulphite.

Further proof of structure is found in the coupling of sulphato-compounds with diazo-salts in the para-position to the sulphatoethyl-amino-group, a position which would not be occupied if sulphonation had taken place. In all such reactions as the formation of nitroso-compounds, indamines, etc., the sulphatoethylarylamines behave like the analogous simple alkylarylamines.

#### EXPERIMENTAL.

*N*-Phenyl- $\beta$ -aminoethyl Hydrogen Sulphate ("Sulphatoethylaniline") (Formula II).—(a) Hydroxyethylaniline (68.5 grams), dissolved in 150 c.c. of tetrachloroethane cooled with ice-water, was slowly treated with 58.0 grams of distilled chlorosulphonic acid with strong stirring during a period of fifteen minutes. The sulphato-compound at once separated as a granular mass, which was stirred for some hours, eventually being warmed to expel the last traces of hydrochloric acid. The solvent was filtered off, the residue thoroughly pressed, and the remainder of the solvent removed by stirring with 100 c.c. of methylated spirit. The yield of dry substance amounted to 100 grams (92 per cent. of theory).

For analysis, the substance was twice crystallised from alcohol, in which it is soluble to the extent of about 5 per cent. at the boiling point and 1–2 per cent. when cold. The crystals are colourless, rectangular laminæ, m. p. 206° (Found: S = 14.69; N = 6.35.  $C_8H_{11}O_4NS$  requires S = 14.74; N = 6.45 per cent.).

In order to prove that all the sulphur is combined as the sulphuric ester, a weighed quantity of the substance was hydrolysed with boiling dilute hydrochloric acid, and the sulphur weighed as barium sulphate (Found: S = 14.69 per cent.).

In aqueous solution sulphatoethylaniline reacts with hypochlorites, giving colour reactions which vary with the temperature and concentration. It decolorises bromine water, but does not react with copper sulphate.

(b) Hydroxyethylaniline (13.7 grams) was dissolved in 27 grams of concentrated sulphuric acid and heated for one hour on the steam-bath. A drop of the solution was then found to be completely soluble in caustic soda. On pouring into 100 grams of ice and water and adding 100 c.c. of saturated salt solution, a white precipitate was obtained. This was collected and dried, and weighed 4.3 grams. It was analysed by conversion to the barium salt and estimation of

the ratio between the figures given by the chromate and *p*-nitrobenzenediazonium chloride titres (Callan and Henderson, *J. Soc. Chem. Ind.*, 1919, **38**, 410r) (Found: ratio diazo-titre/barium = 4.131. Theoretical ratio  $569/137 = 4.154$ ).

The remainder of the sulphatoethylaniline was found in the filtrate from which the solid had been separated, since sufficient basic properties are retained for it to be soluble in strongly acid solution. This solution can be employed, without isolation of the product, for the preparation of azo-derivatives, etc.

(c) A solution of 12.5 grams of the barium salt of  $\beta$ -chloroethyl hydrogen sulphate was heated under reflux with 5.4 grams of barium carbonate and 5 grams of aniline for three hours. The corresponding action between aniline and ethylene chlorohydrin is practically complete in this time, but in this case there remained much undissolved carbonate. The mixture was filtered, the excess of aniline boiled away, the hydroxyethylaniline produced by hydrolysis was extracted with ether, and the solution analysed as above (Found: ratio diazo-titre/barium = 3.908). The total amount in solution showed that the reaction had proceeded to the extent of 37 per cent.

It appears from this and other experiments that the chlorine in  $\beta$ -chloroethyl hydrogen sulphate is more firmly fixed than in ethylenechlorohydrin. The rate of reaction with aniline is only a trifle greater than the rate of hydrolysis of the sulphato-derivative produced and hence the yield is not increased by boiling for many hours, the final products of reaction being barium sulphate and chloride and hydroxyethylaniline.

*Rate of Hydrolysis.*—On account of the relationship of sulphatoethylaniline to ethyl hydrogen sulphate, it was of interest to determine its stability to hydrolytic agents. (a) Stability to acids. The following are the velocity coefficients ( $k \times 1000$ ) which have been determined, using hydrochloric acid. The amount of decomposition was estimated volumetrically and the values of  $k$  found are those for a unimolecular reaction.

Concentration of sulphatoethylaniline and hydrochloric acid, both  $N/5$ .

Temperature 70°.		Temp. of gently boiling solution.	
Time (mins.).	$k$ .	Time (mins.).	$k$ .
120	0.148	125	2.013
180	0.126	242	2.043
240	0.112	365	2.122
360	0.103		

(b) Stability to water alone. When heated alone in aqueous solution, sulphatoethylaniline was found to hydrolyse, but not so quickly as in the presence of hydrochloric acid, and very slowly below the boiling point of the solution.

Concentration of sulphatoethylaniline  $N/5$ . Temperature of gently boiling solution.

Time (mins.) .....	30	120	185	215	365
$k$ .....	0.371	0.381	0.354	0.348	0.350

(c) Stability to alkalis. It was found that when a solution of the sodium salt of sulphatoethylaniline of  $N/5$ -concentration was heated at  $70^\circ$  with caustic soda, either of  $N/5$ - or  $4N/5$ -concentration, practically no hydrolysis had occurred even after five hours.

In a more drastic experiment, 2.271 grams of the sodium salt were heated in a dish with 3 molecules of caustic soda for an hour. Hydrolysis had occurred to the extent of 20.4 per cent. in the semi-solid mass which remained.

*Salts.*—In all properties these salts bear a close resemblance to those of ethyl hydrogen sulphate.

Salt.	Appearance.	Solubility (approx.).	
		Grams per 100 c.c. of solution at $15^\circ$ .	Water of crystallisation (mols.).
Sodium .....	Colourless leaflets	60	One
Potassium .....	" "	23	None
Ammonium .....	" "	70	None
	M. p. $132^\circ$		

*N-o-Tolyl- $\beta$ -aminoethyl Hydrogen Sulphate* ("Sulphatoethyl-*o*-toluidine"),  $C_6H_4Me \cdot NH \cdot C_2H_4 \cdot O \cdot SO_3H$ .—This compound was obtained in somewhat lower yield by acting on hydroxyethyl-*o*-toluidine under the conditions described in (a) above. It resembles sulphatoethylaniline very closely and crystallises in the same form, m. p.  $203^\circ$  (Found: S = 13.78.  $C_9H_{13}O_4NS$  requires S = 13.86 per cent.).

*N-Phenyl-N-ethyl- $\beta$ -aminoethyl Hydrogen Sulphate* ("Sulphatoethyl-ethyl-aniline"),  $C_6H_5 \cdot NEt \cdot C_2H_4 \cdot O \cdot SO_3H$ .—Hydroxyethylethylaniline (82.5 grams) was dissolved in 100 c.c. of tetrachloroethane and 58.0 grams of pure distilled chlorosulphonic acid were dropped in during fifteen minutes with ice cooling and rapid agitation. Hydrogen chloride was given off, and a clear, viscous oil resulted. In one experiment this oil was kept after dilution with alcohol when, after several days, beautiful, white crystals of the sulphato-compound were deposited, but in small yield. It was found that by warming the oily mixture the reaction was rapidly completed, the sulphato-compound separating in hard granules. These were collected, washed with alcohol, and dried. The yield amounted to 88 per cent.

A sample crystallised from alcohol had m. p.  $208^\circ$  (Found: S = 13.02.  $C_{10}H_{15}O_4NS$  requires S = 13.06 per cent.).

*N-p-Nitrosophenyl-N-ethyl-β-aminoethyl Hydrogen Sulphate* ("p-Nitrososulphatoethylethylaniline"),  $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NEt} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{SO}_3\text{H}$ .—Twelve grams of sulphatoethylethylaniline were dissolved in 50 c.c. of *N*-caustic soda, with addition of 3.5 grams of solid sodium nitrite. Ten c.c. of concentrated hydrochloric acid were added slowly, the temperature being maintained at 0–5°. The nitroso-compound separated as a dark green precipitate which, when collected and dried, formed a dark green dust, decomposing at 170–180°. The yield amounted to 10.2 grams (Found: S = 11.37.  $\text{C}_{10}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$  requires S = 11.68 per cent.).

This substance can be readily reduced, best in alkaline solution, giving *as*-sulphatoethylethyl-*p*-phenylenediamine.

Sulphatoethylethylaniline can also be produced from sulphuric acid and hydroxyethylethylaniline in the manner described for ethylsulphatoaniline. The solution so obtained can be used directly for the production of the above nitroso-derivative without isolation of the sulphato-compound.

*N-Phenyl-N-methyl-β-aminoethyl Hydrogen Sulphate* ("Sulphatoethylmethylaniline"),  $\text{C}_6\text{H}_5 \cdot \text{NMe} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{SO}_3\text{H}$ .—When hydroxyethylmethylaniline was acted upon by chlorosulphonic acid in tetrachloroethane solution, a viscous, yellow oil separated. On separating the oil and stirring with alcohol, a portion crystallised. The crystals were collected and recrystallised from 100 c.c. of alcohol. The yield amounted to 32 per cent., the remainder being an oil believed to be the neutral ester. The crystalline sulphato-compound has m. p. 193° (Found: S = 13.86.  $\text{C}_9\text{H}_{13}\text{O}_4\text{NS}$  requires S = 13.82 per cent.).

*Sodium N-Phenyl-N-benzyl-β-aminoethyl Sulphate* (Sodium Salt of "Sulphatoethylbenzylaniline"),  $\text{CH}_2\text{Ph} \cdot \text{NPh} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{SO}_3\text{Na}$ .—From the reaction product of hydroxyethylbenzylaniline and chlorosulphonic acid only a minute amount of a solid melting at 230–231° was isolated.

When 7 grams of hydroxyethylbenzylaniline were heated for an hour at 95° with 13 grams of concentrated sulphuric acid and the mixture poured on ice, a viscous oil separated. This was dissolved in hot dilute caustic soda and, on cooling, shining crystals of the sodium salt separated in high yield. For analysis, this was recrystallised from hot water. The product was air-dried and found to contain two molecules of water of crystallisation. When heated at 100°, the salt sinters to a waxy mass (Found: in anhydrous salt, S = 9.90.  $\text{C}_{15}\text{H}_{16}\text{O}_4\text{NSNa}$  requires S = 9.73 per cent.).

On adding acid to a solution of this salt, a viscous solid was obtained which appeared to be the free acid.

*N-m-Nitrosophenyl-β-aminoethyl Hydrogen Sulphate* ("Sulphatoethyl-m-nitroaniline"),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{SO}_3\text{H}$ .—On acting

on 18 grams of hydroxyethyl-*m*-nitroaniline (m. p.  $41^{\circ}$ , from ether), dissolved in 100 c.c. of tetrachloroethane, with 11.6 grams of chlorosulphonic acid, a cream-coloured solid separated. It was collected, pressed, and crystallised from 150 c.c. of alcohol, 10 grams of stout, needle-shaped crystals being obtained which melted at  $203^{\circ}$  with decomposition (Found: S = 12.39.  $C_8H_{10}O_6N_2S$  requires S = 12.21 per cent.).

The acid, which is of a pale cream colour, dissolves in alkalis to give a deep orange solution when concentrated, the salts crystallising readily in pale yellow crystals. The nitro-group can be reduced easily by warm alkaline hyposulphite to give *as*-sulphatoethyl-*m*-phenylenediamine. The acid also combines with one equivalent of *m*-nitroaniline to give a well-defined salt, stable in acid solution, melting at  $206^{\circ}$  and crystallising from alcohol in large, pale yellow laminæ (Found: S = 8.17.  $C_{14}H_{16}O_8N_4S$  requires S = 7.99 per cent.).

*N*-*p*-Chlorophenyl- $\beta$ -aminoethyl Hydrogen Sulphate ("Sulphatoethyl-*p*-chloroaniline"),  $C_6H_4Cl \cdot NH \cdot C_2H_4 \cdot O \cdot SO_3H$ .—Hydroxyethyl-*p*-chloroaniline (m. p.  $77.5^{\circ}$ , from alcohol) was acted on by an equivalent quantity of chlorosulphonic acid exactly as in the preceding case. The crude product formed a stiff, white, crystal mass. It was crystallised from 250 c.c. of alcohol, giving beautiful, white needles, m. p.  $217^{\circ}$  with decomposition (Found: S = 12.90.  $C_8H_{10}O_4NClS$  requires S = 12.7 per cent.).

*N*- $\alpha$ -Naphthyl- $\beta$ -aminoethyl Hydrogen Sulphate ("Sulphatoethyl- $\alpha$ -naphthylamine"),  $C_{10}H_7 \cdot NH \cdot C_2H_4 \cdot O \cdot SO_3H$ .—18.7 Grams of hydroxyethyl- $\alpha$ -naphthylamine were sulphated in 50 c.c. of tetrachloroethane with 11.6 grams of chlorosulphonic acid. The product separated at once and weighed, when dry, 21 grams. A sample was crystallised from alcohol, in which it is only very sparingly soluble, and the resulting crystals melted at  $234^{\circ}$  with decomposition (Found: S = 11.83.  $C_{12}H_{13}O_4NS$  requires S = 11.99 per cent.).

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THE RESEARCH LABORATORIES,

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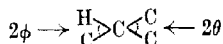
[Received, August 1st, 1922.]

CCCXXII.—*The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part V. Products derived from  $\alpha$ -Halogenated  $\beta$ -Methylglutaric Acids.*

By CHRISTOPHER KELK INGOLD.

IN Part I of this series (T., 1921, 119, 305), the suggestion was made that the angle between any two valencies of a carbon atom is determined by the atomic volumes of the four groups attached. From this hypothesis it followed that the carbon valencies of an unstrained polymethylene chain are inclined, not at  $109.5^\circ$  as Baeyer's theory requires, but  $115.3^\circ$ , and a means was thus found of accounting for the small tendency to the formation of *cyclobutane* rings, the similar stability of *cyclopentane* and *cyclohexane* rings, and the marked effect of two alkyl groups attached to the same carbon atom in promoting the formation of three-, four-, and five-membered homocyclic rings. It is proposed now to examine the effect of a single alkyl group on the ease of closure of these rings.

Adopting the method of calculation previously employed, it is seen that a carbon atom attached to three carbon atoms and one hydrogen atom is to be represented by an irregular tetrahedron having three planes of symmetry:



If  $V$  and  $v$  are the atomic volumes of carbon and hydrogen respectively, the three longer edges of the tetrahedron will enclose a face and be proportional to  $2V^{\frac{1}{3}}$ , whilst the three shorter edges will meet at a vertex and be proportional to  $V^{\frac{1}{3}} + v^{\frac{1}{3}}$ . The angle,  $2\theta$ , between two carbon-to-carbon valencies, and the angle,  $2\phi$ , between a valency attaching carbon and one attaching hydrogen to the central carbon atom will then be given by the following pair of equations:

$$V^{\frac{1}{3}} (\cos \theta - \frac{2}{3}\sqrt{3} \cot 2\phi - 1) + v^{\frac{1}{3}} = (-\frac{1}{3}V^{\frac{1}{3}} + 2V^{\frac{1}{3}}v^{\frac{1}{3}} + v^{\frac{1}{3}})$$

and

$$2 \sin \theta = \sqrt{3} \sin 2\phi$$

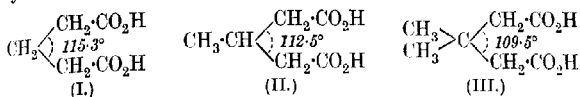
of which the solution for  $\theta$  is

$$\cos \theta = 1 + \frac{\sqrt{3}}{2} \left( \frac{v}{V} \right)^{\frac{1}{3}} \frac{\sqrt{3} V^{\frac{1}{3}} - \sqrt{-V^{\frac{1}{3}} + 6(Vv)^{\frac{1}{3}} + 3v^{\frac{1}{3}} + \sqrt{3}v^{\frac{1}{3}}}}{V^{\frac{1}{3}} - 3v^{\frac{1}{3}}}$$

This equation leads to the value  $2\theta = 112.5^\circ$ , that is, slightly more than the arithmetic mean between the values of the corres-

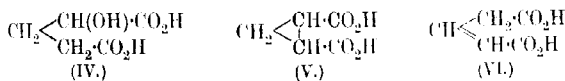
ponding angle in an unsubstituted and in a *gem*-substituted polymethylene chain.

The purpose of this paper is to institute an experimental comparison between glutaric acid,  $\beta$ -methylglutaric acid, and  $\beta\beta$ -dimethylglutaric acid with respect to the manner in which the ease of their transformation into cyclic structures by the interaction of substituents attached to the two acetic acid residues is conditioned by the angles represented in the following formulæ :



It has been shown in preceding parts of this series that one method of obtaining information regarding ease of ring formation from substituted glutaric acids consists in treating their  $\alpha$ -bromoderivatives with alkalis under carefully standardised conditions, when *cyclopropane* ring formation takes place in competition with hydroxylation. The latter process is a side reaction which appears suitable as a standard of reference in estimating ease of ring formation, for it occurs with about the same facility in all the bromoglutaric acids hitherto investigated, so far as can be judged from experiments conducted under a second set of standard conditions chosen in such a way that ring formation becomes inconsiderable and hydroxylation the principal reaction in all cases.

The action of alkalis on the  $\alpha$ -halogen derivatives of glutaric acid itself, under the two sets of standard conditions which have been used throughout this research, was described in Part I, and the general conclusion was drawn that whereas with dilute alkalis (conditions A, T., 1921, 119, 318) almost the whole of the material undergoes the side reaction giving the hydroxy-acid (IV), along with a few units per cent. of the *cyclopropane* acid (V), when concentrated alkalis are used (conditions B, *ibid.*, p. 319) 47 per cent. of the *cyclopropane* acid is produced along with some hydroxy-acid and traces of glutaric acid (VI).



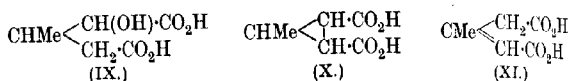
It quickly became clear, when the investigation was extended to  $\beta$ -methylglutaric acid, that derivatives of this substance exhibit a markedly increased tendency to yield derivatives of *cyclopropane*.  $\beta$ -Methylglutaric acid is readily monobrominated in the form of its acid chloride, and the product, on pouring into ethyl alcohol, gives the neutral ester (VII), unaccompanied by any appreciable amount



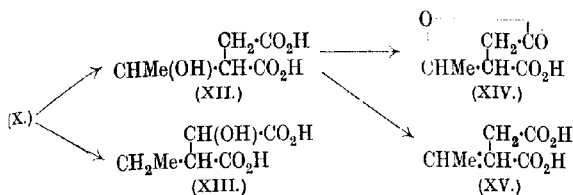
of acid ester (distinction from  $\beta\beta$ -dimethylglutaric acid). Dibromination gives rise to a mixture of two esters, both of which, however, are  $\alpha\alpha'$ -compounds represented by formula (VII). In this case also, only traces of acid esters are produced.



When ethyl  $\alpha$ -bromo- $\beta$ -methylglutarate was treated with dilute alkalis (conditions A) the main product was  $\alpha$ -hydroxy- $\beta$ -methylglutaric acid (IX), which was isolated in the form of its lactone in 90 per cent. yield, along with a small amount (which could not be exactly estimated owing to the character of the separation) of the methylcyclopropane acid (X). On the other hand, when concentrated alkalis were used (conditions B) only 10 per cent. of the hydroxy-acid was formed, the product consisting mainly of the ring acid (X), together with a moderate amount of the normal form of  $\beta$ -methylglutaconic acid (XI):



In addition to these compounds, certain others were isolated, the production of which must be ascribed to consecutive rather than to simultaneous reactions. The principal one of these was methylparaconic acid (XIV), evidently formed through the fission of the cyclopropane ring of the acid (X) to give methylitamic acid (XII), which passes into its lactone on acidification of the solution. A portion of the itamic acid, however, evidently undergoes dehydration in another direction, for methylitaconic acid (XV) can be isolated in small amount. Another by-product was ethylmalic acid (XIII). This must be formed by fission of the ring-acid by the addition of water in reverse direction to that which obtains in the formation of methylitamic acid. The reaction which leads to methylitamic acid has a number of well-known analogies, as, for instance, the formation of terebic acid from caronic acid, but the other mode of fission, leading to ethylmalic acid, is so far without parallel, either in the case of the cyclopropane acid derived from glutaric acid, or in any of the ring acids derived from the  $\beta\beta$ -dialkylglutaric acids which have been investigated up to the present time in this laboratory; it may be peculiar to the arrangement of tertiary carbon atoms present in the molecule of the ring acid (X), and in similarly constituted compounds derived from the  $\beta$ -monoalkylglutaric acids. The relationship between the various fission products may be expressed as follows:



Turning to the quantitative aspect, it is to be noted that, as in certain instances previously described, it was not found possible to account for the whole of the material owing to difficulties attending complete separation, which were particularly great in the present case because the principal product and one of the by-products were liquid acids. The following figures, however, represent the result of the best experiment, and were obtained by employing considerable amounts of material. It may be added, with regard to the deficit of 19 per cent., that all the products, before weighing, were subjected to rigorous purification, during which small losses of material were practically unavoidable, so that when count is taken of the number and character of the processes involved it would seem improbable that any by-product of importance has been overlooked.

TABLE I.

	Per cent.
Lactone of $\alpha$ -hydroxy- $\beta$ -methylglutaric acid .....	8
Normal $\beta$ -methylglutaconic acid .....	9
<i>cis</i> - and <i>trans</i> -3-Methylcyclopropane-1 : 2-dicarboxylic acid .....	53
Methylparaconic acid .....	5
Methylitaconic acid * .....	3
Ethylmalic acid .....	3

Total identified = 81

\* Part of this was isolated as methylcitraconic acid (ethylmaleic acid), into which it was converted during the separation processes.

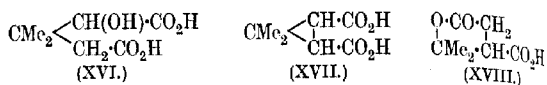
In order to render complete the comparison which forms the subject of this communication, the action of concentrated alkali on ethyl  $\alpha$ -bromo- $\beta\beta$ -dimethylglutarate was examined more carefully than heretofore. Eighty-eight per cent. of the material was accounted for as follows :

TABLE II.

	Per cent.
Lactone of $\alpha$ -hydroxy- $\beta\beta$ -dimethylglutaric acid .....	4
<i>trans</i> -Caronic acid .....	58
<i>cis</i> -Caronic acid .....	22
Terebic acid .....	4

Total identified = 88

The small yield of the hydroxy-acid (XVI) and the large yield of the stereoisomeric ring-acids (XVII) are especially noticeable here. Terebic acid (XVIII) is the normal fission product of caronic acid, but its production in the presence of alkalis has not previously been observed.



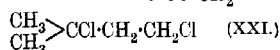
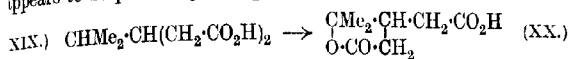
In computing these results for the purpose of arriving at an estimate of the relative tendencies towards ring closure in the three series, we are entitled to count, in place of each fission product of a cyclopropane acid, an equivalent amount of the ring-acid from which it is derived. Dealing in this way with the data of Tables I and II and the table given in Part I (*loc. cit.*), we obtain the following result:

TABLE III.

Products.	Derivatives from		
	Glutaric acid (per cent.).	$\beta$ -Methylglutaric acid (per cent.).	$\beta\beta$ -Dimethylglutaric acid (per cent.).
$\alpha$ -Hydroxyglutaric acids .....	16	8	4
Glutaconic acids .....	3	9	0
cyclopropane acids .....	47	64	84
	66	81	88

The rather considerable yield of  $\beta$ -methylglutaconic acid is worthy of notice at this point. Ethyl  $\alpha$ -bromo- $\beta$ -methylglutarate has previously been converted into  $\beta$ -methylglutaconic acid by heating with diethylaniline, distilling, and hydrolysing the appropriate fraction of a somewhat complex product (Darbishire and Thorpe, T., 1905, 87, 1714). The greater yield of  $\beta$ -methylglutaconic acid obtained in the present experiments, as compared with the yield of glutaconic acid derived from ethyl  $\alpha$ -bromoglutarate, is evidently an indication of the lability of tertiary hydrogen as compared with secondary hydrogen in an otherwise similar situation; for the figures show that the tertiary  $\beta$ -hydrogen atom of  $\beta$ -methylglutaric acid suffers elimination along with the  $\alpha$ -bromine atom much more easily than the secondary  $\beta$ -hydrogen atom of glutaric acid despite the fact that two hydrogen atoms are available in the second case. The oxidation of  $\beta$ -isopropylglutaric acid (XIX) to terpenylic acid (XX) (Lawrence, T., 1899, 75, 531), and the chlorination of isomyl chloride to give, as principal product, the dichloride (XXI) (W. H. Perkin, *J. Soc. Chem. Ind.*, 1912, 31, 621) are instances

of two other types of reaction to which the tertiary hydrogen atom appears to be peculiarly susceptible.



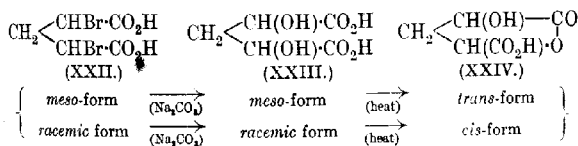
Regarding the *cyclopropane* acids, it is evident that the formation of glutaconic acids in two of the cases constitutes a side reaction which is in no sense standard, and therefore must be viewed, when considering the relation between hydroxylation and ring-formation, merely as a means whereby a certain quantity of material has been "put out of action." The following table shows the proportions of hydroxylation products to ring-acids calculated as percentages of the material identified as having passed into one or other of these two forms:

TABLE IV.

	Derivatives from		
	Glutaric acid.	$\beta$ -Methylglutaric acid.	$\beta\beta$ -Dimethylglutaric acid.
Hydroxylation .....	25	11	5
Ring-formation .....	75	89	95
	100	100	100

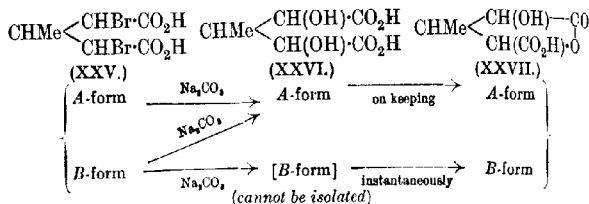
These figures show in a singularly clear manner the effect of introducing one and then a second  $\beta$ -methyl group into derivatives of glutaric acid on the case of their transformation into acids of the *cyclopropane* series.

The comparative examination of the dibromination products of these acids has yielded interesting results. Glutaric acid gives a mixture of two stereoisomeric  $\alpha\alpha'$ -dibromo-acids (XXII) (m. p.  $170^\circ$  and  $142^\circ$ , respectively), the less fusible acid constituting about two-thirds of the mixture. These substances are converted by boiling dilute alkalis into the corresponding  $\alpha\alpha'$ -dihydroxyglutaric acids (XXIII), which, on heating, pass into monolactone acids (XXIV):

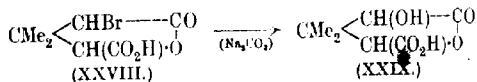


$\beta$ -Methylglutaric acid also gives a mixture of two stereoisomeric dibromo-acids (XXV) (m. p.  $154^\circ$  and  $118^\circ$ , respectively), the less fusible acid forming about two-thirds of the whole product. The

less fusible substance on treatment with sodium carbonate gives a dihydroxy-acid (XXVI), whilst the more fusible form passes into a mixture of isomeric dihydroxy-acids, one of which is the compound derived from the less fusible dibromo-acid. These substances exhibit in a striking way the increasing tendency towards  $\gamma$ -lactone ring formation which one meets on passing from the glutaric acid series to the  $\beta$ -methylglutaric acid series and thence to the  $\beta\beta$ -dimethylglutaric acid series. The two  $\alpha\alpha'$ -dihydroxyglutaric acids mentioned above are moderately stable substances: one of them passes into its lactone at the melting point ( $162^\circ$ ), and the other at temperatures above  $100^\circ$ . On the other hand, the  $\alpha\alpha'$ -dihydroxy- $\beta$ -methylglutaric acids are exceedingly unstable; one of them, indeed, can be isolated, but it passes into its lactone (XXVII) on keeping at the ordinary temperature; the other dihydroxy-acid has not been isolated in the free state and all attempts to obtain it by regeneration from its salts have proved fruitless owing to the ease with which the free acid undergoes lactone formation:

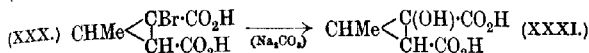


(Non-committal prefixes are used in connexion with these isomerides, because it does not seem possible to assign definite configurations on the basis of the evidence brought forward in this paper.) The tendency to  $\gamma$ -lactone formation is even greater in the *gem*-dimethyl series. Boiling water converts  $\alpha\alpha'$ -dibromo- $\beta\beta$ -dimethylglutaric acid into its lactone (XXVIII), which on treatment with sodium carbonate gives, in place of the dihydroxy-acid, the extremely stable hydroxy-lactone (XXIX), isolated by Perkin and Thorpe (T., 1901, 79, 756):

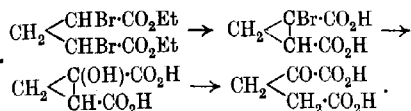


The action of alkalis on the methyl and ethyl esters of  $\alpha\alpha'$ -dibromo- $\beta$ -methylglutaric acid follows an interesting course. In the first place, it must be noted that dilute sodium carbonate gives mainly hydroxylation products accompanied by about 12 per cent. of the bromocyclopropane acid (XXX), which, on continued

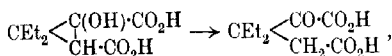
treatment with the same reagent, yields the hydroxy-ring acid (XXXI):



Thus the action of sodium carbonate on the dibromo-esters of  $\beta$ -methylglutaric acid is closely similar to its action on corresponding derivatives of glutaric acid. In the glutaric acid series, however, it was not found possible to produce the hydroxy-ring acid by the action of concentrated methyl alcoholic potassium hydroxide on the dibromo-ester; the actual product of this decomposition consisted to the extent of 70–75 per cent. of  $\alpha$ -ketoglutaric acid, the formation of which was explained as follows:



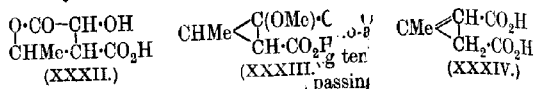
Since each stage of this series of changes can be carried out separately by suitably adjusting the conditions, there seems to be no room for doubt that the above scheme correctly represents the course of the process. As in the methylglutaric acid series, changes corresponding with the first two are known to occur in the presence of dilute alkali, and as the third change is precisely analogous to a reaction in the diethylglutaric acid series recently described by Deshapanda and Thorpe (this vol., p. 1430),\*



it seems at first sight very singular that no trace of any ketonic acid could be found in the product of the action of concentrated alkalis on the dibromo-ester of methylglutaric acid. Apparently the single methyl group and the adjacent tertiary hydrogen atom are responsible for this change in the course of the reaction, the hydroxy-ring acid (XXXI) undergoing fission at the neighbouring bond to give a hydroxy-lactone (XXXII), which, along with a methoxy-ring acid (XXXIII), constitutes the major portion of the yield. In addition, the product contained a few units per cent. of an unsaturated ring acid (XXXIV), which Feist first prepared by the action of alkalis on ethyl bromoisodehydracetate (*Ber.*, 1893,

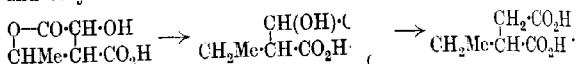
\* There is, to date, evidence of the occurrence of this type of change in two other series, namely, the  $\beta\beta$ -dimethylglutaric and the  $\beta$ -methyl- $\beta$ -ethylglutaric acid series.

26, 747), and a small amount of the hydroxylation products previously mentioned.



The constitution assigned to the series stated acid is not that which Feist originally gave to it, but one at to which a detailed investigation of the substance (shortly to be published) has led. The formation of this substance is strictly analogous to the formation of  $\beta$ -methylglutaconic acid from the  $\alpha$ -bromo-ester, and the fact that isolable quantities are produced although none of the corresponding cyclopropene acid (Farm and Ingold, T., 1921, 119, 2015) could be obtained from the  $\alpha$ -bromo-ester of glutaric acid is in complete harmony with what is written on p. 2680 regarding the tendency to elimination of the tertiary hydrogen atom of  $\beta$ -methylglutaric acid.

It remains to be added that the constitution of the hydroxy-lactone (XXXII) was proved by the formation of ethylmalic acid and ethylsuccinic acid on reduction:—



#### EXPERIMENTAL

The  $\beta$ -methylglutaric acid required for these experiments was obtained by hydrolysing the condensate, a product of acetaldehyde with cyanoacetamide as described by Armstrong and Thorpe (T., 1920, 117, 1469).

##### (A).—Monohalogenation of $\beta$ -methylglutaric Acid.

A mixture of  $\beta$ -methylglutaric acid (800 grams) and thionyl chloride (800 grams) was warmed until more sulphur dioxide was generated. The product was kept at  $-55^\circ$  while dry bromine (460 grams) was added in small portions to keep pace with the absorption.

Methyl  $\alpha$ -bromo- $\beta$ -methylglutarate,  $\text{CO}_2\text{Me} \cdot \text{CHBr} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , was prepared by pouring the crude bromination product into methyl alcohol and collecting in ether after addition of water. Traces of acid products having been removed with aqueous sodium carbonate, the extract was washed with water, dried, and evaporated, the residual oil being carefully fractionated to remove small quantities of unbrominated and dibrominated esters. After five distillations, the monobromo-ester was obtained as an oil, b. p.  $143-145^\circ/12$  mm. (Found: Br = 31.3.  $\text{C}_8\text{H}_{13}\text{O}_4\text{Br}$  requires Br = 31.6 per cent.).

*Ethyl α-bromo-β-methylglutarate* (VII) was prepared like the preceding ester, ethyl alcohol being used in place of methyl alcohol. It boiled at 160°/11 mm. (Found: Br = 28.8. Calc., Br = 28.5 per cent.). This ester has been described previously (Darbishire and Thorpe, *loc. cit.*).

*Methyl α-iodo-β-methylglutarate*,  $\text{CO}_2\text{Me}\cdot\text{CHI}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ .—The methyl bromo-ester was digested for two hours with an alcoholic suspension of an equivalent quantity of finely divided sodium iodide. The oil product which separated on pouring into water was collected in ether and purified by distillation. It boiled at 180°/12–13 mm. (Found: I = 42.2.  $\text{C}_8\text{H}_{13}\text{O}_4\text{I}$  requires I = 42.3 per cent.).

*Ethyl α-iodo-β-methylglutarate*,  $\text{CO}_2\text{Et}\cdot\text{CHI}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained from the ethyl bromo-ester by the action of sodium iodide as in the preceding experiment, boiled at 199–200°/10 mm. (Found: I = 38.3.  $\text{C}_{10}\text{H}_{17}\text{O}_4\text{I}$  requires I = 38.7 per cent.).

(B).—*Dihalogenation of β-Methylglutaric Acid.*

The dibromination was conducted like the monobromination except that twice the proportion of bromine was used and the whole operation conducted at 100°. The product was divided, part being poured into formic acid, part into methyl alcohol, and part into ethyl alcohol.

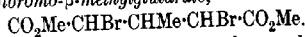
*αα'-Dibromo-β-methylglutaric Acid* (XXV, A form).—The formic acid solution was boiled until the evolution of gaseous products ceased, and then cooled. Even a considerable proportion of the A-dibromo-acid crystallised. The formic acid solution was evaporated and the solid residue obtained from a trace of strongly coloured syrup. The crystals were then boiled with just enough benzene to cover them completely, filtered, shaken for a few moments, and the undissolved material collected on a filter and washed with benzene. The washed crystals, along with the crop obtained from the formic acid solution, were purified by crystallisation first from a mixture of ethyl acetate and chloroform and then from a mixture of ethyl acetate and benzene. The A-dibromo-acid separates from these solvents in prisms, m. p. 153–154°, which appear very dense and strongly refracting. It is fairly soluble in cold ethyl acetate, cold formic acid, or hot chloroform, sparingly soluble in cold chloroform or in hot benzene, almost insoluble in cold benzene, and very soluble in methyl or ethyl alcohol, acetone, or hot ethyl acetate. The yield of pure acid was about 55 per cent. of the theoretical (Found: Br = 52.3.  $\text{C}_6\text{H}_8\text{O}_4\text{Br}_2$  requires Br = 52.6 per cent.).

*αα'-Dibromo-β-methylglutaric acid* (XXV, B form).—The benzene mother-liquors obtained in the above preparation deposited a  
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considerable quantity of the *B*-acid (which separates from solution much more slowly than the *A*-acid) on keeping for twenty-four hours, and a further amount was obtained by evaporation. The acid was purified by repeated crystallisation from benzene, from which it separated in microscopic needles, m. p. 116–118°. It is very soluble in most of the usual organic solvents, but is only sparingly soluble in cold benzene, and insoluble in ligroin (Found: Br = 52.5.  $C_6H_8O_4Br_2$  requires Br = 52.6 per cent.).

*Methyl  $\alpha\alpha'$ -Dibromo- $\beta$ -methylglutarate,*



—The preparation of this ester from the crude dibromination product with the aid of methyl alcohol was similar to that of the monobromo-ester. It boiled at 179–180°/20 mm., the yield being 90 per cent. of the theoretical (Found: Br = 48.0.  $C_8H_{12}O_4Br_2$  requires Br = 48.2 per cent.).

*Ethyl  $\alpha\alpha'$ -dibromo- $\beta$ -methylglutarate* (VIII), also obtained in 90 per cent. yield by pouring the dibromination product into ethyl alcohol, boiled at 189–190°/28–29 mm. (Found: Br = 44.4.  $C_{10}H_{16}O_4Br_2$  requires Br = 44.4 per cent.).

(C).—*Action of Dilute Alkalis on Ethyl  $\alpha$ -Bromo- $\beta$ -methylglutarate: Formation of the Lactone of  $\alpha$ -Hydroxy- $\beta$ -methylglutaric Acid and trans-3-Methylcyclopropane-1:2-dicarboxylic Acid.*

Twenty-five grams of ethyl  $\alpha$ -bromo- $\beta$ -methylglutarate (section A) were boiled with 4.5 equivalents of 2*N*-aqueous sodium carbonate for twenty hours. The product was acidified with concentrated hydrochloric acid, and the solution extracted three times with an equal volume of ether. The aqueous layer was evaporated to dryness and the residue extracted with dry acetone.

*Lactone of  $\alpha$ -Hydroxy- $\beta$ -methylglutaric Acid,*  $\begin{matrix} CH_2 \cdot CO \cdot O \\ | \\ CHMe - CH \cdot CO_2H \end{matrix}$

—The acetone extract yielded almost pure lactone on evaporation, whilst the ethereal solution gave a mixture of the lactone with *trans*-3-methylcyclopropane-1:2-dicarboxylic acid, which was separated by the method described below. On distillation, the lactone was obtained as a colourless, rather viscous liquid, b. p. 189–190°/45 mm. (Found: C = 50.2; H = 5.6.  $C_6H_8O_4$  requires C = 50.0; H = 5.5 per cent.).

The ammonium salt separated from a small amount of methyl alcohol in rosettes of needles (Found: C = 44.2; H = 7.1.  $C_6H_{11}O_4N$  requires C = 44.7; H = 6.8 per cent.). The silver salt, prepared from the ammonium salt, separated in needles from aqueous solution (Found: Ag = 42.9.  $C_6H_7O_4Ag$  requires Ag = 43.0 per cent.).

*α-Hydroxy-β-methylglutaric Acid (IX).*—This acid does not appear to be stable in the free state, but its salts are formed when the lactone is dissolved in excess of alkalis. Attempts to regenerate the acid led to the lactone.

The *barium* salt, prepared by boiling the lactone with two equivalents of barium hydroxide and evaporating the solution, forms leaflets which disintegrate on drying at 120° (Found: Ba = 46.0.  $C_6H_8O_5Ba$  requires Ba = 46.2 per cent.). The *silver* salt was prepared from the barium salt (Found: Ag = 57.1.  $C_6H_8O_5Ag_2$  requires Ag = 57.5 per cent.).

*trans-3-Methylcyclopropane-1:2-dicarboxylic Acid (X).*—The residue from the ether extract (above) was digested in a shaking machine for twenty-four hours with an excess of precipitated calcium carbonate. The filtered solution was evaporated to dryness and the calcium salt recrystallised from a concentrated aqueous solution of calcium chloride. The acid regenerated from the calcium salt agreed closely in its properties with the description given by Kötze and Stahlmann (*J. pr. Chem.*, 1903, [ii], **68**, 159), and its identity was further confirmed by converting it into the anhydride of methylcitraconic acid (ethylmaleic acid) by dry distillation (Found: C = 50.0; H = 5.7. Calc., C = 50.0; H = 5.5 per cent.).

The *calcium* salt (above) forms small leaflets which were dried at 120° before analysis (Found: Ca = 22.0.  $C_6H_6O_4Ca$  requires Ca = 22.0 per cent.). The *silver* salt was prepared from the calcium salt and dried at 120° (Found: Ag = 60.0.  $C_6H_6O_4Ag_2$  requires Ag = 60.3 per cent.).

The *anhydride* of *cis-3-methylcyclopropane-1:2-dicarboxylic acid*,  $CHMe \begin{matrix} \diagup CH \cdot CO \\ \diagdown CH \cdot CO \end{matrix} O$ , was obtained by heating the *trans*-acid with an excess of acetic anhydride at 180° for six hours. The anhydride was isolated by distillation and thus obtained as a colourless oil, b.p. 270° (Found: C = 57.0; H = 4.9.  $C_6H_6O_3$  requires C = 57.1; H = 4.8 per cent.).

*cis-3-Methylcyclopropane-1:2-dicarboxylic acid\* (X).*—This acid, which has been described previously by Preisweck (*Ber.*, 1903, **36**, 1087), was obtained by boiling the anhydride with water and

\* Three isomeric 3-methylcyclopropane-1:2-dicarboxylic acids are theoretically possible. A third acid, m.p. 132°, can be isolated in small amount from the "low" fraction obtained during the distillation of the anhydride (Found: C = 50.6; H = 5.5.  $C_6H_8O_5$  requires C = 50.0; H = 5.5 per cent.). The *trans*-acid described by Kötze and Stahlmann as a liquid is actually a solid, m.p. 165°, which is very hygroscopic when slightly impure. Further experiments on this and other acids of the cyclopropane series have been undertaken by Mr. F. R. Goss, of this College.

evaporating. It melted at  $108^{\circ}$ , and agreed in properties with Preissweck's description; its identity was further confirmed by converting it into methylitaconic acid by heating with water in a sealed tube (Found: C = 50.3; H = 5.5. Calc., C = 50.0; H = 5.5 per cent.).

The calcium salt crystallised from a concentrated aqueous solution in small leaflets which were dried at  $120^{\circ}$  (Found: Ca = 22.1.  $C_6H_6O_4Ca$  requires Ca = 22.0 per cent.). The silver salt was obtained as a curdy precipitate by adding silver nitrate to a solution of the calcium salt (Found: Ag = 60.1.  $C_6H_6O_4Ag_2$  requires Ag = 60.3 per cent.).

(D).—*Action of Concentrated Alkalis on Ethyl  $\alpha$ -Bromo- $\beta$ -methylglutarate: Formation of the Lactone of  $\alpha$ -Hydroxy- $\beta$ -methylglutaric Acid, 3-Methylcyclopropane-1:2-dicarboxylic Acid,  $\beta$ -Methylglutaconic Acid, Methylparaconic Acid, Methylitaconic Acid, and Ethylmalic Acid.*

The bromo-ester (211 grams) (section A) was heated to  $100^{\circ}$ , and poured into 1000 c.c. of boiling, pure 6*N*-methyl-alcoholic potassium hydroxide. The product was evaporated several times with water and again with hydrochloric acid, and the organic acids extracted from the dried residue with acetone. The residue from the acetone was shaken for twenty-four hours with an aqueous suspension of precipitated calcium carbonate, and the filtered solution evaporated to a small bulk, saturated with calcium chloride, and allowed to crystallise. The calcium salts were washed with saturated calcium chloride solution, and the combined filtrate and washings worked up for organic acids, which were converted into their ammonium salts, and thence into their silver salts. The latter were digested for sixteen hours with an alcoholic solution containing an excess of benzyl iodide, and the filtered solution was poured into water and extracted with ether.

*$\alpha$ -Hydroxy- $\beta$ -methylglutaric Acid (IX).*—The residue from the ether was distilled up to a temperature of  $240^{\circ}/16$  mm., and the distillate boiled with an excess of 2*N*-ethyl-alcoholic potassium hydroxide. The product was worked up for organic acids in the usual way, and the syrup so obtained boiled for a short time with an excess of *p*-toluidine. The product which separated on pouring the solution into dilute hydrochloric acid was crystallised from alcohol, and then boiled with 50 per cent. sulphuric acid until no crystals separated on cooling and diluting. The lactone of the hydroxy-acid was isolated by extracting the solution with a large quantity of ether (Found: C = 50.3; H = 5.6 per cent.).

The *di-p-toluidide*,  $\text{CHMe} \begin{array}{l} \text{CH(OH)CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7 \\ \text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7 \end{array}$ , obtained in the above process, separated from alcohol in leaflets, m. p. 235–236°, and was identified with a specimen prepared from the pure lactone (Found: C = 70.5; H = 7.3.  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2$  requires C = 70.6; H = 7.1 per cent.).

*Methylitamic Acid* (XII).—When the more soluble *di-p-toluidides*, which were obtained in the course of the above separation, were hydrolysed with 50 per cent. sulphuric acid and the acids extracted with ether, a syrup was produced which yielded crystals on rubbing with benzene. These consisted of methylparaconic acid, which gave salts of methylitamic acid on treatment with excess of alkalis.

The *barium* salt ( $\text{C}_6\text{H}_8\text{O}_5\text{Ba}\cdot 3\text{H}_2\text{O}$ , Fittig, *Annalen*, 1889, 255, 18) was dried at 150° before analysis (Found: Ba = 45.9. Calc., Ba = 46.2 per cent.).

*Methylparaconic Acid* (XIV).—The crystalline lactone on crystallisation from benzene melted at 78–79°, and agreed in its properties with Fittig's description (*loc. cit.*) of methylparaconic acid. It was identified by analysis, and by its conversion into methylcitraconic acid (Found: C = 50.0; H = 5.8. Calc., C = 50.0; H = 5.5 per cent.).

*Methylitaconic Acid* (XV).—The less volatile benzyl esters (above) were hydrolysed with 2*N*-ethyl alcoholic potassium hydroxide, and the recovered acids were decolorised with charcoal and boiled with chloroform, which caused crystals of methylitaconic acid to separate. After crystallisation from water, the acid melted at 166° and had the properties ascribed to it by Fittig (*loc. cit.*) (Found: C = 49.7; H = 5.7. Calc., C = 50.0; H = 5.5 per cent.). It was further identified by conversion into methylcitraconic acid.

*Ethylmalic Acid* (XIII).—This acid, which remained dissolved in the boiling chloroform, partly separated on cooling, and a further quantity was obtained by fractionally crystallising the product contained in the mother-liquor. After a final crystallisation from a mixture of ether and chloroform, the acid melted at 108–109°, and closely corresponded with the description given by Lütz (*Ber.*, 1902, 35, 4372) (Found: C = 44.4; H = 6.1. Calc., C = 44.4; H = 6.2 per cent.).

*cis-3-Methylcyclopropane-1:2-dicarboxylic Acid* (X).—The more soluble acid, which was separated from ethylmalic acid with the aid of chloroform (a further quantity was obtained from the ultimate residues by rubbing with benzene), proved to be the *cis*-ring acid, and was identified by analysis, and by a mixed-melting-point determination with the specimen prepared (section C) from the

*trans*-isomeride (Found: C = 49.9; H = 5.5. Calc., C = 50.0; H = 5.5 per cent.).

*trans*-3-Methylcyclopropane-1:2-dicarboxylic Acid (X).—The acids regenerated from the less soluble calcium salts were boiled with six times their weight of acetyl chloride, and the product, after evaporation of the acetyl chloride, distilled up to 150°/10 mm. in a current of dry air. The less volatile portion was cooled, mixed with benzene, and treated with a small amount of aniline. After twenty-four hours, the solution was filtered and the acids therein isolated. Final purification was effected through the calcium salt as described in section C (Found: C = 50.0; H = 5.7. Calc., C = 50.0; H = 5.5 per cent.).

*Normal*  $\beta$ -Methylglutaconic Acid (XI).—The volatile anhydrides were shaken for a few seconds with cold dilute sodium carbonate, and the acids regenerated from the aqueous layer. The acid so obtained, which was purified by crystallisation from concentrated hydrochloric acid, was identified, by its melting point, 149°, by analysis (Found: C = 50.3; H = 5.7. Calc., C = 50.0; H = 5.5 per cent.), and by direct comparison with a genuine specimen, as the less fusible form of  $\beta$ -methylglutaconic acid.

The *anilic acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPh}$ , obtained during the purification of the *trans*-ring acid, was purified by crystallisation from a mixture of benzene and acetone. Its identity was confirmed by the melting point (143°), by analysis (Found: C = 65.7; H = 5.9. Calc., C = 65.8; H = 5.9 per cent.), and by a mixed-melting-point determination with an authentic specimen.

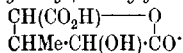
*cis*-Methylcitraconic Acid,  $\text{CO}_2\text{H}\cdot\text{CEt}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ .—The oily anhydrides were boiled with water for a short time and the solution was distilled in a current of steam. The distillate was rendered alkaline with sodium carbonate and evaporated to dryness. The residue was dissolved in a small amount of hydrochloric acid and extracted with ether, and the acid thus obtained crystallised from water, from which it separated in dense prisms, m. p. 100–101° (decomp.), having all the properties of methylcitraconic acid. It was identified by analysis (Found: C = 50.0; H = 5.1. Calc., C = 50.0; H = 5.5 per cent.), by its characteristic calcium and barium salts, which are more soluble in cold water than hot, and by conversion into methylitaconic acid by heating with water in a sealed tube.

The acids which remained in the distilling flask consisted largely of *cis*-3-methylcyclopropane-1:2-dicarboxylic acid, which does not appear to undergo anhydride formation below 100°.

(E).—*Action of Dilute Alkalis on the  $\alpha\alpha'$ -Dibromo- $\beta$ -methylglutaric Acids and their Esters: Formation of meso- and racemic  $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acids, their Lactonic Acids, and 1-Bromo- and 1-Hydroxy-3-methylcyclopropane-1:2-dicarboxylic Acids.*

(a) *Hydrolysis of the A-Dibromo-acid*.—Twenty-one grams of the A-acid (section B) were boiled with 200 c.c. of 2*N*-aqueous sodium carbonate for one and a half hours, and the solution was acidified with hydrochloric acid and evaporated to dryness. The residue was extracted with acetone, and the exhausted solid material re-evaporated with hydrochloric acid and again extracted. The residue from the acetone (10 grams) completely solidified after a few days.

*Lactone of A- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acid,*



—The preceding solid melted at 128–134° without purification, and therefore consisted almost solely of the A-lactone, which separated from a large volume of dry ether in short, stout, rhombic prisms with nearly square ends, m. p. 136–136.5°. It is readily soluble in acetone, methyl or ethyl alcohol, and in water, sparingly soluble in ether, and almost insoluble in benzene or chloroform (Found: C = 44.6; H = 5.3.  $\text{C}_6\text{H}_8\text{O}_5$  requires C = 45.0; H = 5.0 per cent.). The same lactone was also obtained from the B-bromo-acid (below).

*A- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acid (XXVI).*—When an aqueous solution of the above lactone was allowed to evaporate at the ordinary temperature, a residue was obtained which consisted of the dihydroxy-acid (Found: C = 40.7; H = 5.6.  $\text{C}_6\text{H}_{10}\text{O}_6$  requires C = 40.5; H = 5.6 per cent.). The acid crystallises in plates which melt at 80°, giving the lactone, to which the acid slowly reverts on keeping at the ordinary temperature.

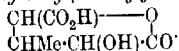
The *barium* salt, which was obtained by evaporating a solution of the acid or its lactone in two equivalents of barium hydroxide, crystallised in leaflets. It was dried at 150° (Found: Ba = 44.0.  $\text{C}_6\text{H}_8\text{O}_6\text{Ba}$  requires Ba = 44.0 per cent.). The *silver* salt was precipitated from a solution of the barium salt (Found: Ag = 54.7.  $\text{C}_6\text{H}_8\text{O}_6\text{Ag}_2$  requires Ag = 55.1 per cent.).

The *di-p-toluidide*,  $\text{CHMe}[\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4]_2$ , was prepared by boiling the lactone with an excess of *p*-toluidine for a few seconds. The *p*-toluidide crystallised on cooling and was purified by trituration with dilute hydrochloric acid, and crystallisation from a mixture of alcohol and acetone. It separated in needles, which melted at 207° and were only sparingly soluble in hot ethyl

alcohol (distinction from the *B*-toluidide) (Found: C = 67.3; H = 6.8.  $C_{20}H_{24}O_4N_2$  requires C = 67.4; H = 6.7 per cent.).

(b) *Hydrolysis of the B-Dibromo-acid*.—This acid was hydrolysed like the *A*-acid, and the product isolated in the same way. It solidified after a year, and was then fractionally crystallised from dry ether, by which means a considerable quantity of the *A*-lactone (m. p. 136°) was readily isolated.

*Lactone of B- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acid,*



—This is more soluble in ether than the *A*-lactone, and was obtained in a pure condition only after many crystallisations. It separates from ether in minute granules, m. p. 117–118° (Found: C = 4.50; H = 5.2.  $C_6H_8O_5$  requires C = 45.0; H = 5.0 per cent.).

*B- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acid (XXVI)*.—This substance appears to be stable only in the form of its salts, and all attempts to prepare it in the free state, either by regeneration from its salts or from the lactone, proved fruitless.

The *barium* salt, prepared from the lactone and two equivalents of barium hydroxide, forms minute rosettes of needles. The salt was dried at 150° before analysis (Found: Ba = 43.6.  $C_6H_8O_6Ba$  requires Ba = 44.0 per cent.). The *silver* salt, prepared from the barium salt, forms microscopic needles (Found: Ag = 54.9.  $C_6H_8O_6Ag_2$  requires Ag = 55.1 per cent.).

The *di-p-toluidide*,  $\text{CHMe}[\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{C}_7\text{H}_7]_2$ , was prepared from the lactone and *p*-toluidine, and was purified by crystallisation from alcohol, in which it is readily soluble (distinction from the *A*-toluidide). It forms long needles, m. p. 187° (Found: C = 67.1; H = 6.6.  $C_{20}H_{24}O_4N_2$  requires C = 67.4; H = 6.7 per cent.).

(c) *Hydrolysis of the Methyl and Ethyl Dibromo-esters*.—One decigram-molecule of either ester was boiled with 250 c.c. of a 2*N*-solution of sodium carbonate for twenty hours and the solution acidified with 50 c.c. of concentrated hydrochloric acid and extracted with 3 litres of ether. The aqueous residue was then evaporated to dryness and extracted with acetone.

*A- and B- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acids (XXVI)*.—The residue from the acetone evidently consisted almost entirely of these dihydroxy-acids or their lactones, as on boiling with excess of *p*-toluidine it gave twice its weight of a mixture of two *p*-toluidides, which were readily separated by crystallisation from alcohol, and identified as the *A*- and *B*-toluidides described above.

*1-Bromo-3-methylcyclopropane-1:2-dicarboxylic Acid (XXX)*.—The ethereal extract yielded on evaporation a crystalline residue which melted at 180–190°, and, after two crystallisations from

chloroform containing a trace of ether, at 190–191°. The acid, which is microcrystalline, is stable towards alkaline permanganate, and the presence of halogen could not be detected by heating in an open tube with nitric acid and silver nitrate (Found: C = 32.3; H = 3.6; Br = 35.3.  $C_6H_7O_4Br$  requires C = 32.3; H = 3.2; Br = 35.9 per cent.). The estimation of bromine in the acid is difficult on account of its great stability; the result quoted was obtained after heating with fuming nitric acid and silver nitrate at 330–350° for twenty-four hours (compare T., 1921, **119**, 325).

The silver salt also is remarkably stable and can be boiled with water for hours without darkening. The silver was therefore estimated by precipitation with hydrochloric acid (Found: Ag = 49.3.  $C_6H_5O_4BrAg_2$  requires Ag = 49.4 per cent.).

*3-Methylcyclopropan-1-ol-1:2-dicarboxylic Acid* (XXXI).—This acid was prepared from the bromo-acid by boiling for a month with a 2N-solution of sodium carbonate, and was isolated by extraction with acetone after evaporating the acidified solution to dryness. The solid product was boiled with dry ether and the insoluble portion crystallised several times from a mixture of acetone and benzene. The acid separated in minute needles, m. p. 167–169°; it appears to be stable towards boiling hydrochloric acid, boiling dilute alkalis, and cold alkaline permanganate (Found: C = 45.2; H = 5.3.  $C_6H_8O_5$  requires C = 45.0; H = 5.0 per cent. For the silver salt: Found: Ag = 57.4.  $C_6H_8O_5Ag_2$  requires Ag = 57.7 per cent.).

(F).—*Action of Concentrated Alkali on Ethyl  $\alpha\alpha'$ -Dibromo- $\beta$ -methylglutarate: Formation of A- and B- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acids, their Lactonic Acids, the Lactone of Butane- $\alpha\gamma$ -diol- $\alpha\beta$ -dicarboxylic Acid, 1-Methoxy-3-methylcyclopropane-1:2-dicarboxylic Acid, and Methylcyclopropenedicarboxylic Acid.*

The dibromo-ester (360 grams) was heated at 100°, and poured into 1800 c.c. of 6N-methyl-alcoholic potassium hydroxide, the experimental conditions being similar to those employed in the case of dibromoglutaric ester. On extracting the acid products, two syrups were obtained, one readily soluble in dry ether (147 grams), and the other sparingly soluble in ether but easily soluble in acetone (5 grams).

*A- and B- $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric Acids* (XXVI).—The syrup insoluble in dry ether consisted principally of a mixture of the lactonic acids of these two hydroxy-acids. They were separated in the form of their *p*-toluidides as described in section (E).

*Methylcyclopropenedicarboxylic Acid* (XXIV).—The syrup which was soluble in ether was esterified with ethyl alcohol and sulphuric



acid, and the esters were isolated in the usual way, the acid products being separated from the neutral and re-esterified. The combined neutral esters were then subjected to a careful fractionation under diminished pressure with the aid of a short column of beads. The pressure was maintained accurately at 35 mm. during the distillation by means of a hand-controlled regulator consisting of a pipe-clay tube different lengths of which can be exposed above mercury. After seven distillations it became evident that no further advantage was to be gained by continuing the process, the material having been fairly completely resolved into three nearly constant-boiling liquids, and a small quantity of comparatively non-volatile material, the investigation of which was abandoned. The most volatile fraction, b. p. 130—135°, and the middle fraction, b. p. 141—143°, on hydrolysis with hydrochloric acid both gave a mixture of crystalline acids which were separated by crystallisation from water and from a mixture of chloroform and benzene. The *cyclopropene* acid was identified by its melting point (200°), by analysis (Found: C = 50.5; H = 4.4. Calc., C = 50.7; H = 4.2 per cent.), and by direct comparison with an authentic specimen.

*1-Methoxy-3-methylcyclopropane-1:2-dicarboxylic Acid* (XXXIII).—This acid, which was separated from the unsaturated acid in the way mentioned, crystallises from a mixture of chloroform and benzene in needles, m. p. 102—104°. It is very soluble in chloroform, methyl or ethyl alcohol, ethyl acetate, or acetone, and sparingly soluble in ether or benzene. It does not decolorise cold alkaline permanganate (Found: C = 48.2; H = 6.1.  $C_7H_{10}O_5$  requires C = 48.3; H = 5.8 per cent.).

*Butane-xy-diol- $\alpha\beta$ -dicarboxylic Acid* (Monolactone, XXXII).—The lactone of this acid was obtained by acid hydrolysis of the fraction of b. p. 168—171°, but it could not be induced to solidify and was therefore purified by crystallisation of the calcium and barium salts of the dihydroxy-acid. The free dihydroxy-acid does not appear to be capable of existence, and attempts to prepare it from the salts proved fruitless.

The *calcium* salt was prepared by digesting a solution of the barium salt with precipitated calcium sulphate, and evaporating the filtered solution. The salt took a considerable time to solidify, but the drained material crystallised well from concentrated aqueous solution on addition of acetone (Found: Ca = 18.5.  $C_6H_8O_6Ca$  requires Ca = 18.5 per cent.). The *barium* salt, prepared from the lactone and barium hydroxide, was obtained as minute needles (Found: Ba = 44.1.  $(C_6H_8O_6)Ba$  requires Ba = 44.0 per cent.).

The *ethyl* ester is a colourless liquid, b. p. 168—171°/35 mm.

(Found: C = 51.1; H = 7.9.  $C_{10}H_{18}O_6$  requires C = 51.3; H = 7.7 per cent.).

The *lactonic acid*, prepared by decomposing the calcium or barium salt with mineral acids, was obtained as a viscous gum which showed no tendency to crystallise (Found: C = 45.2; H = 4.9.  $C_6H_8O_5$  requires C = 45.0; H = 5.0 per cent.). Its acetyl and benzoyl derivatives were also gummy, but the composition of the substance and of the silver, calcium, and barium salts described in this section, taken in conjunction with the reduction products mentioned below, appears to leave no room for doubt as to its constitution.

The *silver salt* was prepared from a concentrated neutral solution of the ammonium salt, and was recrystallised from hot water (Found: C = 26.6; H = 2.8; Ag = 40.2.  $C_6H_7O_5Ag$  requires C = 27.0; H = 2.6; Ag = 40.4 per cent.).

*Reduction of Butan- $\alpha\gamma$ -diol- $\alpha\beta$ -dicarboxylic Acid to Ethylmalic Acid and Ethylsuccinic Acid.*—The lactonic acid was boiled for twenty-four hours with an excess of distilled hydriodic acid and the product extracted with ether. The syrupy residue partly solidified on keeping for several months in an evacuated desiccator over potassium hydroxide, and was then drained as completely as possible on porous porcelain. The crystalline material melted over a large interval of temperature, and was easily separated by trituration with a little cold water into two main fractions. The less soluble acid, after purification, melted at  $98^\circ$  and was identified as ethylsuccinic acid (Found: C = 49.2; H = 7.1. Calc., C = 49.3; H = 6.9 per cent.), whilst the more soluble proved to be ethylmalic acid, and was identified as such by direct comparison and by a mixed-melting-point determination with the product previously obtained (section D).

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## CCCXXIII.—1:3:4:6-Tetramethyl Fructose.

By JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON.

It is now well known that the ketose constituent of sucrose and of inulin is entirely different from the characteristic levorotatory sugar known as *D*-fructose. On the other hand, the best-defined artificial derivatives of fructose are related to the ordinary variety of the sugar and do not possess the same structural unit as the natural fructosides. For example, it has been shown that  $\beta$ -methylfructoside (Steele, T., 1918, 103, 257), fructosediacetone and fructosemonoacetone (Irvine and Patterson, this vol., p. 2146) have no relationship with  $\gamma$ -fructose, as they are each convertible into the levorotatory crystalline form of tetramethyl fructose.

Two isomeric tetramethyl fructoses are known and these substances function as reference compounds which serve to identify the particular type to which a fructose derivative belongs. For some time it has been felt necessary to have fuller information regarding the properties and structures of the isomeric tetramethyl fructoses, as otherwise it is difficult, particularly in the  $\gamma$ -series, to formulate derivatives satisfactorily. We have accordingly extended the earlier investigation of crystalline tetramethyl fructose and compared the chief properties of the compound with those of the  $\gamma$ -isomeride prepared from inulin.

Considering the objects in view, it was necessary to commence the preparation of the sugar from a crystalline derivative of fructose which is known to belong to the stable series. For this purpose, tetra-acetyl fructose was selected and, although the conversion of the compound into the corresponding tetramethyl derivative is laborious, the result was satisfactory. In the experimental part, an account is given of the isolation of the sugar and of its conversion into the pure  $\alpha$ -form, the corrected physical constants for which are quoted. These agree closely with the values found by Purdie and Paul (T., 1907, 91, 289), but it may be mentioned that with the larger quantity of material at our disposal we succeeded in separating a second variety of tetramethyl fructose which crystallised in slender needles showing no mutarotation.

In comparison with tetramethyl  $\gamma$ -fructose, the normal crystalline isomeride melting at 98–99° may be described as stable. This is shown in many reactions as, for example, the condensation with methyl alcohol to give the corresponding fructosides. Under parallel conditions, the two sugars reacted with the solvent at widely different speeds, tetramethyl  $\gamma$ -fructose requiring only twenty-four hours for complete condensation, whereas with levorotatory tetra-

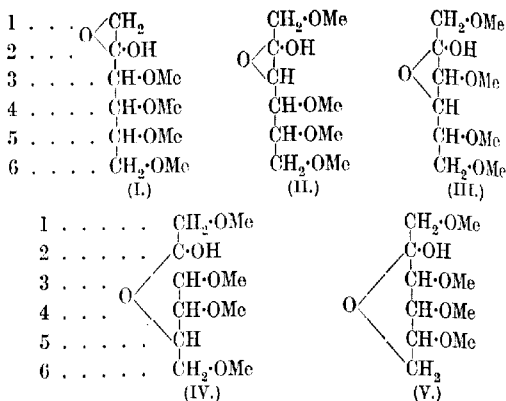
methyl fructose the same reaction occupied about seventy days. In a similar manner, it has been shown that tetramethyl  $\gamma$ -methylfructoside was much more readily hydrolysed than the levorotatory isomeride. This pronounced difference in reactivity is also emphasised when the rate of hydrolysis of  $\beta$ -methylfructoside is compared with that of  $\gamma$ -methylfructoside (Menzies, this vol., p. 2238).

The reactions just referred to, although useful in discriminating between the different types of fructose derivatives, give no clear indication as to structural distinctions. Information on this point was, however, obtained by studying the behaviour of the sugars towards oxidising media. Neutral potassium permanganate had practically no effect on crystalline tetramethyl fructose, but reacted readily with the  $\gamma$ -isomeride. It is, however, probable that this action is due to the presence of traces of impurity and is not a characteristic of  $\gamma$ -sugars, as reduction of the reagent practically ceased when less than one atomic proportion of oxygen was utilised, and the sugar recovered after this treatment had no effect on the reagent. The application of alkaline permanganate as an oxidising reagent was complicated by the fact that both varieties of tetramethyl fructose react with alkali. In the case of tetramethyl  $\gamma$ -fructose, the action was extremely rapid and when the sugar was dissolved in *N*/10-sodium hydroxide the activity quickly altered from dextro to laevo. In the parallel case of the stable isomeride, solution in alkali gave a pronounced exaltation in the levorotation, but the value diminished irregularly in the course of several days.

The action of alkaline permanganate appears to involve enolisation and rupture of the ketose molecules between the second and third carbon atoms of the chain, with the result that only one definite product was isolated. This proved to be the potassium salt of a dimethoxyhydroxybutyric acid. The use of dilute nitric acid as the oxidising medium proved to be more satisfactory. The reagent has already been applied to tetramethyl  $\gamma$ -fructose and, in the case of the crystalline isomeride, gave a dimethoxyhydroxyglutaric acid as the essential product. This was isolated in the form of the corresponding diethyl ester, and the bearing of the combined results on the constitution of the sugars concerned is given in the discussion which follows.

#### *Discussion of Results.*

Five formulæ differing in the position of the internal oxygen ring may be assigned to a reducing tetramethyl fructose, and the linkage may be determined if the four methoxyl groups can be allocated. These formulæ are :

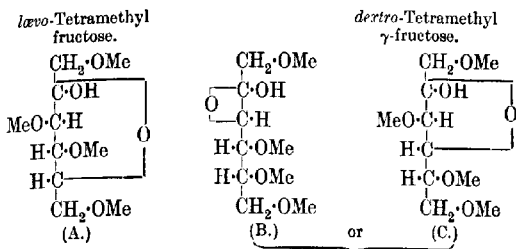


In the particular case under consideration, no methyl group can be present in the 2-position and one of the methyl groups must occupy position 6 as the sugar has been prepared from 6-monomethyl fructose. Formula V can thus be deleted.

Further, the production of a dimethoxyhydroxybutyric acid by the action of alkaline permanganate indicates that this reagent effects rupture of the ketose between positions 2 and 3. This result eliminates formula I and shows that one of the methyl groups removed in the oxidation must be attached to position 1. Having allocated two of the methyl groups, it is evident that the remaining two may occupy any pair of the positions 3, 4, and 5. In deciding between formulae II, III, and IV, the crucial reaction is the formation of dimethoxyhydroxyglutaric acid by the agency of nitric acid. This oxidation involves the conversion of the  $\text{CH}_2 \cdot \text{OMe}$  group in the 6 position into  $\text{CO}_2\text{H}$ , and experience gained in carrying out the same oxidation process on different types of alkylated sugars has shown that a dibasic acid is not readily formed when the group  $\cdot\text{CH}(\text{OMe})\text{CH}_2 \cdot \text{OMe}$  terminates the sugar chain. The formation of a dibasic acid in the present instance is thus unfavourable to formulae II and III. We therefore select formula IV for crystalline tetramethyl fructose, leaving II or III to represent tetramethyl  $\gamma$ -fructose.

In discussing the alternatives for the  $\gamma$ -form the evidence available is somewhat inconsistent, but, so far as chemical reactions are concerned, is more favourable to C than to B. The action of nitric acid on the sugar has already been shown to give trimethoxyhydroxyvaleric acid (Haworth, T., 1920, 117, 199), a result which is consistent with either of the alternative formulae. Moreover, the

structure of  $\gamma$ -fructose derivatives must accommodate the inability of the parent sugar to react with acid acetone and here again both formulæ are equally suitable.



In the course of our researches on inulin, we have been engaged in studying the effect of various oxidising media on the methylated  $\gamma$ -fructoses and find that tetramethyl  $\gamma$ -fructose is acted upon by alkaline potassium permanganate to give a dimethoxybutyrolactone. This reaction, viewed by itself, appears to be diagnostic and favours formula C, which is also in agreement with the structure assigned by Böeseken to the fructose unit in sucrose (*Rec. trav. chim.*, 1921, **40**, 354). Other factors have, however, to be taken into account. For example, the reversal of the sign of rotation encountered in passing from a normal fructose derivative to the  $\gamma$ -type or vice versa cannot be ignored in a formula. This factor is best accounted for by formula B, where configuration demands that the oxygen ring is formed on the opposite side of the carbon chain. In the meantime, no definite decision between these formulæ appears to be warranted, but we are continuing the study of the subject by examining the reactions of trimethyl  $\gamma$ -fructose.

#### EXPERIMENTAL.

##### *Preparation of Tetramethyl Fructose.*

It was found that by far the most convenient starting material for preparing crystalline tetramethyl fructose in quantity is the  $\beta$ -methylfructoside isolated by Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1216). The fructoside was fully methylated as described by Steele (*loc. cit.*) and the tetramethyl methylfructoside thus obtained was then hydrolysed, giving good yields of the alkylated ketose. Full experimental details need not be given, as the operations involved are well standardised, but the following observations indicate various modifications which were introduced with advantage.

*Stage I. Preparation of Tetra-acetyl Fructose.*—The initial period of the acetylation of fructose is a critical stage. Unless the tem-

perature is kept low at the beginning of the reaction, the fructose dissolves rapidly and the main product is the syrupy triacetyl derivative identified by Steele. This diversion of the reaction was largely avoided if, during the first fifteen minutes, stirring was done very slowly. The reaction was thus kept under control and rise of temperature was avoided.

*Stage II. Tetra-acetyl  $\beta$ -Methylfructoside.*—The amount of silver oxide necessary for this reaction is considerably less than that recommended by Hudson. Thus, in one typical experiment, 30 grams of powdered tetra-acetyl fructose were methylated in the presence of 270 grams of methyl iodide by the addition of only 40 grams of silver oxide. Part of the acetyl compound was undissolved at the beginning of the reaction, but gradually passed into solution as methylation proceeded. The product crystallised at once on nucleation, and the yield was practically quantitative.

*Stage III. Deacetylation of Tetra-acetyl  $\beta$ -Methylfructoside.*—The removal of the acetyl groups by the use of barium hydroxide is tedious in large-scale working as, in order to avoid hydrolysis of the fructosidic methyl group, the barium sulphate has to be precipitated and filtered in the cold. In subsequent preparations, Fischer's method for removing acetyl groups was substituted with advantage. A typical example is described.

26.5 Grams of tetra-acetyl methylfructoside were dissolved in 800 c.c. of dry methyl alcohol, and dry ammonia was passed to saturation at 0°. After standing over-night, the solvent and the ammonia were removed under diminished pressure and the dry syrupy residue was extracted with cold acetone to remove acetamide. The residue was dissolved in absolute alcohol, and the solution evaporated to a small bulk. On nucleation, crystals of methylfructoside separated. These were filtered, washed with cold acetone, dried, and recrystallised from hot absolute alcohol. Yield 70 per cent.

*Stage IV. Methylation of  $\beta$ -Methylfructoside.*—Three successive methylations were given, in the first of which a small quantity of methyl alcohol was used as an extraneous solvent. In the subsequent alkylations the material was fully soluble in methyl iodide. The final product, isolated in the usual manner, boiled at 105–107°/0.35 mm. Yield 88 per cent.

*Stage V. Hydrolysis of Tetramethyl  $\beta$ -Methylfructoside.*—The final reaction was conducted without any departure from the customary practice and no difficulty was experienced in obtaining the sugar crystalline. Yield—practically quantitative.

*Properties of 1 : 3 : 4 : 6-Tetramethyl Fructose.*

After six successive crystallisations from low-boiling petroleum the physical constants showed no further variation and the pure  $\alpha$ -form of the sugar was obtained. Crystalline form: square plates; m. p. 98–99°. The accumulated mother-liquors slowly deposited a more soluble variety in elongated, pointed prisms melting at 92°. This may represent the  $\beta$ -isomeride, but no definite upward mutarotation in the *lævo* sense was detected and an alcoholic solution showed at once the constant value  $[\alpha]_D -85.7^\circ$ .

*Mutarotation of the  $\alpha$ -Form.*

Solvent.	c.	Initial $[\alpha]_D^{20}$ .		Permanent $[\alpha]_D^{20}$ .	Time.
Water .....	1.802	$-124.3^\circ$	$\rightarrow$	$-123.2^\circ$	2 hours
Ethyl alcohol .....	2.102	$-94.0$	$\rightarrow$	$-87.7$	3 days
Benzene .....	1.507	$-116.6$	$\rightarrow$	$-84.7$	7 "

As already recorded by Purdie and Paul (T., 1907, 91, 289), the optical change was practically instantaneous in aqueous solution.

*Action of Sodium Hydroxide.*—A 1.634 per cent. solution of the sugar in N/10-aqueous sodium hydroxide showed an initial optical exaltation which diminished irregularly until the darkening of the solution prevented further observations.

Time.	$[\alpha]_D^{20}$ .	Time.	$[\alpha]_D^{20}$ .
3 minutes .....	$-145.6^\circ$	20 days .....	$-90.8^\circ$
20 hours .....	$-141.1$	25 " .....	$-60.0$
44 " .....	$-130.6$	30 " .....	$-44.8$
3 days .....	$-120.2$	40 " .....	$-33.1$

The disruption of the sugar was apparently catalysed by contact with the fittings of the polarimeter tubes, as a duplicate solution which was preserved in a stoppered flask showed a distinct optical lag ( $[\alpha]_D^{20}$  after forty days  $-83^\circ$ ).

*Condensation of 1 : 3 : 4 : 6-Tetramethyl Fructose with Methyl Alcohol.*

A 2.5 per cent. solution of the sugar in pure dry methyl alcohol containing 0.25 per cent. of hydrogen chloride was preserved at 17°, polarimetric readings being taken every twelve hours for a period of seventy-two days. A parallel experiment with tetramethyl  $\gamma$ -fructose, prepared from inulin, emphasises the different reactivities of these isomerides.

Time from start.	Crystalline t-tetramethyl fructose.	Tetramethyl $\gamma$ -fructose.
4 minutes .....	$-96.4^\circ$	$\pm 21.9^\circ$
20 " .....	$-95.6$	$\pm 19.6$
200 " .....	$-95.2$	$\pm 39.5$
1 day .....	$-97.0$	$\pm 50.1$ condensation complete.
6 days .....	$-102.4$	$\pm 59.9$ (constant)
10 " .....	$-105.0$	"
50 " .....	$-128.0$	"
72 " .....	$-134.4$ (constant)	"



*Oxidation of 1 : 3 : 4 : 6-Tetramethyl Fructose.*

1. *Neutral Potassium Permanganate.*—To 100 c.c. of a 1 per cent. aqueous solution of the sugar 10 c.c. of *N*/10-potassium permanganate were added. As the colour of the reagent persisted for twenty days no appreciable oxidation took place.

2. *Alkaline Potassium Permanganate.*—One hundred c.c. of a 3 per cent. solution of the sugar were mixed with a solution of 6 grams of potassium permanganate in 500 c.c. of water. 25 c.c. of *N*-potassium hydroxide were then added and by the following morning the reagent had been completely reduced. Carbon dioxide was passed through the liquid, which was filtered and evaporated to dryness under diminished pressure. An acetone extract of the residue yielded a small quantity of a neutral syrup which contained OMe = 42.9 per cent., and reduced permanganate instantly. The material undissolved by acetone was extracted with absolute alcohol to remove soluble potassium salts and, after fractional precipitation with ether, the product had the composition K = 20.3; OMe = 26.3 per cent. These figures agree most closely with those required for a potassium dimethoxyhydroxybutyrate [ $C_4H_8O_3(OMe)_2K$  requires K = 19.3; OMe = 30.7 per cent.]. The rupture of the ketose to give an oxidation acid containing four carbon atoms in the chain was confirmed in the following reaction.

3. *Nitric Acid.*—A 7 per cent. solution of the sugar in dilute nitric acid (*d* 1.2) was heated at 90° for one hour and thereafter at 80–85° for four and a half hours. Reaction proceeded smoothly, but ceased entirely at temperatures lower than 80°. Excess of nitric acid was removed by maintaining the solution at 40°/15 mm. while water was continually introduced until 1500 c.c. had collected in the receiver. The evaporation was then continued in a stream of alcohol until one litre had distilled, after which the liquid was taken to dryness and heated, first at 40°/0.3 mm. and then at 55°/0.3 mm. until constant in weight. On raising the bath to 130°/0.25 mm., the product was readily distilled as a clear mobile liquid which rapidly crystallised. After spreading on porous porcelain and two recrystallisations from light petroleum, the pure ester was obtained. *M. p.* 86–87°;  $n_D$  1.4643 (Found: C = 49.86, 49.81; H = 7.60, 7.62.  $C_{11}H_{20}O_7$  requires C = 50.00; H = 7.57 per cent.). In this particular case, the determination of methoxyl is not diagnostic, but as the compound possessed the reactions of an alkyloxy-ester it is identified as diethyl dimethoxyhydroxy-glutarate.

4. *Bromine.*—A concentrated aqueous solution of the sugar was shaken for two days with excess of bromine water and then treated as described by Irvine and Hynd (*T.*, 1909, 95, 1220). No organic

acid was, however, produced in the reaction and the sugar was recovered unchanged in the crystalline form.

*Relative Stability of the Isomeric Methylfructosides.*

Although the relative speeds of hydrolysis of tetramethyl methylfructoside and the corresponding  $\gamma$ -isomeride are known, similar data are lacking in the case of the unsubstituted fructosides. It has now been established that when dissolved in  $N/110$ -hydrochloric acid  $\beta$ -methylfructoside possesses a constant rotation for several days. The fructoside is, however, slowly attacked by the reagent and the laevorotation diminished.

Time .....	0	7	15	70 days
$[\alpha]_D$ .....	-172.0°	-169.1°	-162.3°	-136.0°

The development of moulds in the solution prevented a complete polarimetric record being taken, but the optical changes are evidently due to slow hydrolysis. Under parallel conditions,  $\gamma$ -methylfructoside is hydrolysed much more rapidly, the solution changing from dextro to laevo in thirty hours. The experimental details of the oxidation of tri- and tetra-methyl  $\gamma$ -fructose are reserved for inclusion in a forthcoming paper on the structure of inulin.

We desire to express our indebtedness to the Department of Scientific and Industrial Research for generous assistance.

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# CCCXXIV.—*The Oxidation of Sucrose by Nitric Acid.*

By FREDERICK DANIEL CHATTAWAY and HINTON JOHN HARRIS.

FOR over a hundred and fifty years the action which takes place when sucrose is oxidised by nitric acid has attracted the attention of chemists, and its spectacular character, from the torrents of nitrogen peroxide evolved, still makes it a favourite laboratory experiment. It has considerable historical interest, for it was from the product of this action that Bergman ("Opuscula Physica et Chemica," Vol. 1, p. 238. *De acido Sacchari*) about 1776 first isolated oxalic acid. From the testimony of several of his friends, it appears that Scheele had identified the acid shortly before, though whether he obtained it from sugar or from wood sorrel is not clear, for he never published any account of his work. For a

long time, Bergman's process was in everyday use for making oxalic acid, but apparently no very detailed account of it was published until Thompson (*Pharm. J.*, 1848—1849, 8, 117) took up the subject about 1848 and described what he had found to be the most satisfactory procedure.

Since that time, little close attention has been directed to the subject, and oxalic acid has been generally regarded as the sole end-product.

A re-examination of the reaction, however, has shown that, in addition to oxalic acid, mesoxalic acid is formed in considerable quantity and that the violent oxidation of sugar by nitric acid is the most advantageous way of preparing this little-known compound.

Mesoxalic acid is easily detected, being a ketonic acid and forming a well-characterised hydrazone with any aromatic hydrazine. It can be isolated conveniently by making use of the sparing solubility in water of its sodium salt.

About 11 grams of sodium mesoxalate can be obtained from the oxidation of 100 grams of sugar, about 40 grams of crystallised oxalic acid being at the same time produced.

Mesoxalic acid is formed in approximately equal amount when dextrose, levulose, lactose, maltose, or starch is similarly violently oxidised by nitric acid.

#### EXPERIMENTAL.

When powdered or granulated sucrose is added to about fourteen times its weight of strong nitric acid, it dissolves at the ordinary temperature. On slowly heating the solution, it assumes a pale yellow tint which gradually deepens to a light and finally to a dark brown, owing to the formation of oxides of nitrogen. When the temperature reaches 72—75°, vigorous action sets in and if external heating be now stopped the temperature rises rapidly to about 94—95°. This violent action continues for some time and the liquid appears to boil vigorously from the rapid disengagement of nitric oxide, nitrogen peroxide, and carbon dioxide. The temperature remains at first approximately constant, but gradually falls as the action diminishes in violence and finally apparently ceases.

If other proportions of sugar and nitric acid are used or the liquid is heated with varying degrees of rapidity, violent action commences at slightly different temperatures, but the highest temperature reached without further external heating does not much exceed 94—95°. If fuming nitric acid is used, violent action begins of itself after some ten minutes' standing at the ordinary temperature without any preliminary heating. Neither the exact

amount of strong acid initially used nor its exact strength much affects the phenomena observed, and the oxidation of the sugar into simple products is by no means complete when violent action subsides. Further oxidation, however, takes place on again heating and oxalic and mesoxalic acids are now the main products. On cooling the suitably concentrated liquid, the bulk of the oxalic acid crystallises out, and a large part of the excess of nitric acid still remaining can be got rid of as sodium nitrate by the addition of an appropriate amount of solid sodium carbonate. Mesoxalic acid is present in the residual acid liquid in considerable quantity and separates as its sodium salt after complete neutralisation. In order to get consistent results, a definite procedure has to be carefully followed, as even trifling variations, such, for example, as evaporating in a flask instead of an evaporating dish and thus prolonging the heating, much affect the yield of mesoxalate.\*

The following has been found the best method for preparing and isolating sodium mesoxalate. To 50 grams of sucrose in a 1500 c.c. flask are added 700 grams of nitric acid (*d* 1.41), and the mixture is heated to about 72–75°. The source of heat is removed, the violent action allowed to subside—this usually takes about twenty-five minutes—and the liquid poured into an evaporating dish and boiled rapidly until, when cooled to 74°, it occupies a volume of 112 c.c.† The liquid is now transferred to a flask and cooled with constant shaking to –5°. The oxalic acid, which separates and usually amounts to about 21 grams, is filtered by the aid of the pump, using a Buchner funnel and at least three filter-papers or better an asbestos pad. The filtrate is again placed in the evaporating basin and 50 grams of anhydrous sodium carbonate are added in three portions; this causes the temperature to rise to about 70°. The solution is cooled to –5° and the sodium nitrate which separates and usually amounts to about 50 grams is filtered off. To the filtrate 12 grams of anhydrous sodium carbonate are added and then a saturated aqueous solution of

\* The addition of vanadium pentoxide, as recommended by Naumann, Moeser, and Lindenbaum (*J. pr. Chem.*, 1907, [ii], 75, 146), which causes the oxidation of sugar by nitric acid to take place at a lower temperature with a consequent larger yield of oxalic acid if a limited amount of nitric acid is used, causes complete oxidation of the sugar to carbon dioxide if the quantities of nitric acid and sugar given above are employed, so that on evaporation no residue is left.

† During the evaporation the temperature of the boiling liquid rises from about 107° to 111°, and the hot liquid, when poured into a cylinder for measurement, usually cools to very near 74°. It is essential that the volume at 74° should be exactly 112 c.c. as the amount of free acid remaining after partial neutralisation which determines the subsequent separation of the mesoxalate in good yield depends almost entirely on this.

sodium carbonate until the liquid reacts distinctly alkaline; about 40 c.c. of the solution are usually required. The liquid which while acid is pale yellow in colour becomes pale brown when alkaline. The alkaline liquid is kept for twenty-four hours, when 5–6 grams of sodium mesoxalate separate as a colourless, crystalline powder. About a further gram remains dissolved in the alkaline mother-liquor and can be recovered as hydrazone.

The sodium mesoxalate,  $C(OH)_2(CO_2Na)_2$ , thus obtained is practically pure. Two grams of a specimen of the salt thus prepared yielded 2.26 grams of mesoxalic acid phenylhydrazone, the theoretical amount being 2.3 grams.

The hydrazone thus obtained melted with decomposition in one minute when kept at a constant temperature of  $166^\circ$ . When placed in a bath at  $166^\circ$  and heated moderately rapidly, it melted with decomposition at about  $173^\circ$ .

It was moderately easily soluble in boiling alcohol, acetone, or chloroform, and sparingly soluble in boiling water, from all of which it crystallised in pale yellow, slender, flattened prisms. To complete its identification with the hydrazone first prepared by Fischer and Elbers (*Ber.*, 1884, **17**, 578), it was completely analysed (Found: C = 51.8; H = 3.78; N = 13.67. Calc. for  $C_9H_8O_4N_2$ , C = 51.91; H = 3.87; N = 13.46 per cent.).

It was also compared and found to be identical with the hydrazone prepared from specimens of mesoxalic acid obtained from uric acid and from malonic acid.

#### *Oxidation of other Carbohydrates by Concentrated Nitric Acid.*

The other common carbohydrates, dextrose, levulose, lactose, maltose, and starch also yield mesoxalic acid when violently oxidised by nitric acid.

Using the quantities of carbohydrate and nitric acid given above, the phenomena observed are very similar to those noted when sucrose is employed and the yields of oxalic acid and sodium mesoxalate are approximately the same, the amount of oxalic acid crystallising out being roughly two-fifths of the weight of carbohydrate used and that of sodium mesoxalate about one-tenth.

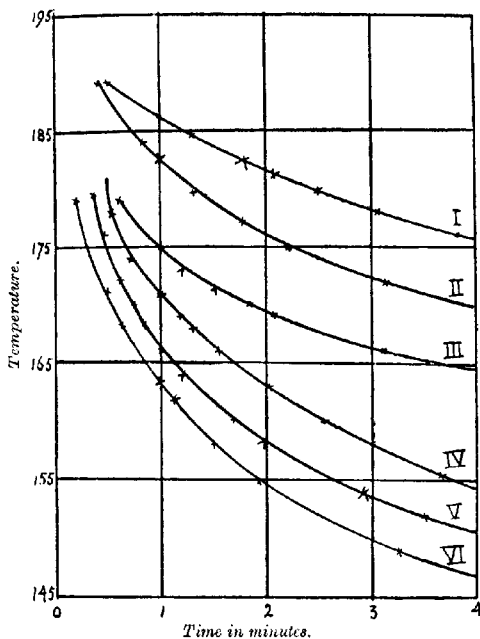
There are, however, considerable differences in the temperatures at which the initial violent reaction starts and in those reached during this action, but otherwise the procedure and results are much the same.

#### *Hydrazones of Mesoxalic Acid.*

The hydrazones of mesoxalic acid are easily made by dissolving sodium mesoxalate in warm water, adding the equivalent quantity

of the hydrazine dissolved in acetic acid, and heating for a few minutes until the solid which is first formed and which appears to be a sparingly soluble hydrazine salt of mesoxalic acid dissolves and a clear liquid results. On cooling and adding excess of hydrochloric acid, the hydrazone of mesoxalic acid separates as a bright yellow solid.

FIG. 1.



- I. Mesoxalic acid p-chlorophenylhydrazone.
- II. Mesoxalic acid 2:4-dichlorophenylhydrazone.
- III. Mesoxalic acid o-chlorophenylhydrazone.
- IV. Mesoxalic acid p-tolylhydrazone.
- V. Mesoxalic acid phenylhydrazone.
- VI. Mesoxalic acid o-tolylhydrazone.

When these hydrazones are heated, they melt with decomposition at temperatures which vary within very wide limits according to the time taken in heating. The actual melting point of any specimen therefore depends on the duration of heating, and to be of any use as a criterion of purity the time of heating as well as the temperature at which liquefaction occurs needs to be given.

In order, therefore, to obtain comparable results the hydrazones

were kept at a number of constant temperatures in the neighbourhood of the melting point, and the time taken before melting at each particular temperature was noted. Melting-point tubes of about 1 mm. internal diameter were filled to a depth of 5 mm. with the powdered hydrazone. At first a rough reading was taken to give an idea of the temperature required. A tube containing the hydrazone was then placed in an oil-bath at the particular temperature and simultaneously a stop-watch was started which was stopped at the moment when the hydrazone melted. Three observations were made at each temperature and the mean taken.

The lowest temperature at which observations were made was in each case that at which the hydrazone would remain during three or four minutes before melting. The curves in the appended figure show the results.

In the case of the bromohydrazones, the points of melting were not sufficiently well defined to be worth recording.

The arylhydrazones of mesoxalic acid are all yellow, well-crystallised compounds, moderately soluble in hot organic solvents such as alcohol, acetic acid, and chloroform, but sparingly soluble in boiling water.

*Mesoxalic acid p-chlorophenylhydrazone*,  $(\text{CO}_2\text{H})_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , crystallises in bright yellow, elongated prisms. If it is kept at a constant temperature of  $186.5^\circ$ , it first shrinks and then melts in one minute. If placed in a bath at  $186^\circ$  and moderately rapidly heated, it melts with decomposition at  $192\text{--}193^\circ$  (Found: Cl = 14.67.  $\text{C}_9\text{H}_7\text{O}_4\text{N}_2\text{Cl}$  requires Cl = 14.62 per cent.).

*Mesoxalic acid o-chlorophenylhydrazone* crystallises in bright yellow, elongated prisms. If it is kept at a constant temperature of  $175^\circ$ , it melts in one minute. If placed in a bath at  $175^\circ$  and heated moderately rapidly, it melts with decomposition at  $183^\circ$  (Found: Cl = 14.35.  $\text{C}_9\text{H}_7\text{O}_4\text{N}_2\text{Cl}$  requires Cl = 14.62 per cent.).

*Mesoxalic acid 2:4-dichlorophenylhydrazone*,  
 $(\text{CO}_2\text{H})_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ ,  
 crystallises in bright yellow, elongated prisms. If it is kept at a constant temperature of  $182.5^\circ$ , it melts with decomposition in one minute. Placed in a bath at  $182.5^\circ$  and heated moderately rapidly, it melts with decomposition at  $188^\circ$  (Found: Cl = 25.42.  $\text{C}_9\text{H}_5\text{O}_4\text{N}_2\text{Cl}_2$  requires Cl = 25.60 per cent.).

*Mesoxalic acid p-bromophenylhydrazone*,  $(\text{CO}_2\text{H})_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ , crystallises in bright yellow, long, slender prisms. When heated, it shrinks, turns brown, and decomposes without previously melting (Found: Br = 27.74.  $\text{C}_9\text{H}_7\text{O}_4\text{N}_2\text{Br}$  requires Br = 27.84 per cent.).

*Mesoxalic acid 2 : 4-dibromophenylhydrazone,*  
 $(\text{CO}_2\text{H})_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Br}_2$ ,

crystallises in bright yellow, very much elongated prisms. When heated moderately rapidly, it melts with decomposition at about  $205^\circ$  (Found: Br = 43.56.  $\text{C}_9\text{H}_6\text{O}_4\text{N}_2\text{Br}_2$  requires Br = 43.68 per cent.).

*Mesoxalic acid p-tolylhydrazone*,  $(\text{CO}_2\text{H})_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in pale yellow, short, flattened prisms. If it is kept at a constant temperature of  $170.5^\circ$ , it melts with decomposition in one minute. Placed in a bath at  $170.5^\circ$  and heated moderately rapidly, it melts with decomposition at  $178^\circ$  (Found: C = 54.13; H = 4.57; N = 12.82.  $\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$  requires C = 54.04; H = 4.54; N = 12.61 per cent.).

*Mesoxalic acid o-tolylhydrazone* crystallises in bright yellow, slender prisms. If it is kept at a constant temperature of  $163.5^\circ$ , it melts with decomposition in one minute. Placed in a bath at  $163.5^\circ$  and heated moderately rapidly, it melts with decomposition at  $171-172^\circ$  (Found: C = 54.33; H = 4.64; N = 12.5.  $\text{C}_{10}\text{H}_{10}\text{O}_4\text{N}_2$  requires C = 54.04; H = 4.54; N = 12.61 per cent.).

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### CCCXXV.—*The Diazo-reaction in the Carbazole Series.* *Carbazole-3-diazoimine and -3-diazonium Salts.*

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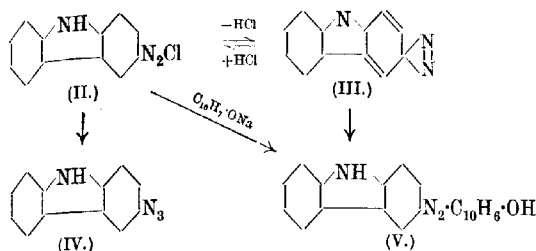
ALTHOUGH carbazole has become increasingly important in recent years as an intermediate in the production of synthetic dyes, comparatively little has been published in regard to its diazo-derivatives, yet obviously the diazotisation of 3:3'-diamino-carbazole has been practised in the manufacture of carbazole yellow.

The diazonium chloride obtained from 3-aminocarbazole is first mentioned by Ruff and Stein (*Ber.*, 1901, **34**, 1668), who, however, did not isolate the substance, but studied it only in aqueous solution. Accordingly, we resolved to investigate further the properties of this and similar diazonium salts of the carbazole series.

The outstanding features in regard to carbazole-3-diazonium salts are (1) their stability compared with the corresponding diazo-derivatives of the benzene, diphenyl, and naphthalene series; (2) their pronounced yellow colour. In the latter respect, the carbazole-3-diazonium salts resemble the similarly constituted

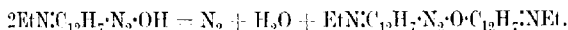
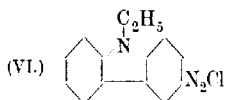






By loss of hydrogen chloride, the yellow *carbazole-3-diazonium chloride* (II) passes into the orange-red quinonoid *carbazole-3-diazoimine* (III), the reaction being reversed when the latter compound is treated with hydrochloric acid. The diazonium chloride and the diazoimine give rise to the same *azo-β-naphthol* derivative (V), the latter process being one of simple addition of *β-naphthol* to the diazoimine. Other *azo-derivatives* can be produced additively by employing other phenols or reactive aromatic amines.

The formation of *carbazole-3-diazoimine* depends on the intervention of the hydrogen of the imino-group, for when this labile atom is replaced by ethyl as in *N-ethylcarbazole-3-diazonium chloride* (VI) the reaction with ammonia takes an entirely different course. Half the diazo-nitrogen is eliminated and the ill-defined solid product which separates has the attributes of an external diazo-oxide, for on treatment with concentrated hydrochloric acid it regenerates the diazonium chloride and yields a greenish-blue product, probably arising from the oxidation of 3-hydroxy-*N*-ethylcarbazole :



#### EXPERIMENTAL.

Carbazole was converted into *N*-nitroso-3-nitrocarbazole by the method of Ruff and Stein (*loc. cit.*) and this nitrated nitrosoamine was reduced to 3-aminocarbazole by means of alcoholic sodium sulphide (Schwalbe and Wolff, T., 1911, 99, 105), the overall yield being 52 per cent.

*Carbazole-3-diazonium chloride*,\*  $\text{C}_{12}\text{H}_8\text{N}_3\text{Cl}\cdot 2\text{H}_2\text{O}$ , was pre-

\* During the course of these experiments, we learnt confidentially that this diazonium salt had been prepared by Dr. S. H. Tucker, and we have accordingly refrained from any detailed investigation of the substance.

pared by adding 20 per cent. aqueous sodium nitrite to a thin paste of 3-aminocarbazole hydrochloride in dilute hydrochloric acid at 8°; the hydrochloride dissolved and the diazonium chloride crystallised from the filtered solution on cooling to 0°. The product, when recrystallised from warm water, separated in fan-shaped clusters of yellow needles which became green at 98° and decomposed at 102°. When dried in a vacuum desiccator over sulphuric acid, the dihydrated diazonium chloride lost its water of crystallisation and assumed an orange-yellow colour. The anhydrous diazonium chloride darkened at 106–110° and decomposed explosively at 153°. The hydrated diazonium chloride gave on analysis the following data:—N = 15.67; Cl = 13.38; H<sub>2</sub>O = 13.26. C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>Cl·2H<sub>2</sub>O requires N = 15.82; Cl = 13.38; H<sub>2</sub>O = 13.56 per cent. The yellow, anhydrous salt, after drying over sulphuric acid for four weeks, gave N = 18.01; Cl = 15.69. C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>Cl requires N = 18.30; Cl = 15.46 per cent.

*Carbazole-3-diazonium aurichloride*, C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>·N<sub>2</sub>AuCl<sub>4</sub>, a bright yellow, sparingly soluble compound, was obtained anhydrous on drying at the ordinary temperature in a vacuum desiccator (Found: Au = 36.50, 37.22. C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>Cl<sub>4</sub>Au requires Au = 36.98 per cent.). The yellow diazonium salts from 3-aminocarbazole were quite stable in the dark, but darkened on exposure to light. During the diazotisation of 3-aminocarbazole hydrochloride a green, insoluble by-product was observed from which by extraction with ether, long, golden-yellow needles of *N*-nitrosocarbazole were obtained melting at 82° (Found: N = 14.07. C<sub>12</sub>H<sub>8</sub>ON<sub>2</sub> requires N = 14.20 per cent.).

*Carbazole-3-diazoimine* (Formula III).—According to the observations of Ruff and Stein, addition of aqueous sodium hydroxide to a solution of carbazole-3-diazonium chloride gave a red coloration and a separation of oily drops changing to a voluminous precipitate of red needles. Analyses gave no definite indications, but these investigators inclined to the view that this product was the free diazo-hydroxide, C<sub>12</sub>H<sub>8</sub>N<sub>3</sub>·N<sub>2</sub>·OH. Our experiments indicated, however, that the insoluble product was in reality the internal diazoimine, which was best obtained pure by adding with stirring 1 c.c. of concentrated ammonia to 0.3 gram of carbazole-3-diazonium chloride dissolved in 10 c.c. of water, both solutions being cooled to 0°. A precipitate of bright orange-red needles separated, and soon the mixture became almost solid. The product was prepared, washed with ice-water, collected in subdued light, and dried in a blackened vacuum desiccator over concentrated sulphuric acid [Found: C = 74.02; H = 4.09; N = 21.85 (total 99.96). C<sub>12</sub>H<sub>7</sub>N<sub>3</sub> requires C = 74.61; H = 3.66; N = 21.76. C<sub>12</sub>H<sub>7</sub>ON<sub>3</sub> requires

C = 68.25; H = 4.26; N = 19.90 per cent.]. These data prove that the substance is *carbazole-3-diazoimine*, and not the diazo-hydroxide.

When heated rapidly, carbazole-3-diazoimine darkened at 80–90° and exploded at 95°, but when the temperature was raised very slowly it began to darken at 80°, was dark brown at 105°, and the residue did not then melt below 300°. The diazoimine was extremely photo-sensitive; it decomposed almost immediately in sunlight, but was comparatively stable in the dark. It exploded on rubbing or by percussion or when placed near a flame. In water, it gave a deep red solution, but all attempts to recrystallise the diazoimine led to decomposition and the formation of a brown insoluble material not melting below 300°; this ill-defined product was similar to the discoloured substance produced by the action of light.

The constitution assigned to the red diazoimine was confirmed by the action of hydrochloric acid, which regenerated yellow carbazole-3-diazonium chloride. Carbazole-3-diazoimine combined additively with phenols and reactive aromatic amines to yield azo-derivatives identical with those produced by coupling with carbazole-3-diazonium chloride. Mixed melting points showed in each case that the two preparations gave identical products.

*Carbazole-3-azo-β-naphthol* (Formula V).—(a) From carbazole-3-diazoimine: equivalent proportions of the diazoimine and β-naphthol were mixed and moistened with alcohol, when the reddish-violet azo-derivative was formed immediately. After washing with aqueous sodium hydroxide, the product was crystallised from glacial acetic acid, when reddish-violet needles separated, melting and decomposing at 277–278° (Found: N = 12.10.  $C_{22}H_{15}ON_3$  requires N = 12.46 per cent.).

(b) From carbazole-3-diazonium chloride by coupling with alkaline β-naphthol: the product, when crystallised from glacial acetic acid, gave reddish-violet needles melting and decomposing at 279° (Found: N = 12.84 per cent.). This azo-β-naphthol developed with concentrated sulphuric acid a bright red coloration changing to violet on exposure.

*Carbazole-3-azoresorcinol*,  $C_{12}H_8N \cdot N_2 \cdot C_6H_3(OH)_2$ .—(a) A mixture of carbazole-3-diazoimine and resorcinol in molecular proportions gave no reaction until moistened with alcohol, when an intensely violet azo-derivative was produced. When dissolved in glacial acetic acid and precipitated therefrom by water, the substance melted at 265–270°.

(b) The same compound was produced by coupling carbazole-3-diazonium chloride and alkaline resorcinol (m. p. 264–268°). Sulphuric acid gave a deep yellow coloration.

*Carbazole-3-azo-β-naphthylamine*,  $C_{12}H_8N \cdot N_2 \cdot C_{10}H_6 \cdot NH_2$ , was obtained on moistening with alcohol a mixture of carbazole-3-diazoimine and β-naphthylamine; it crystallised from alcohol in reddish-brown needles melting at 260–263°. This compound was identical with the preparation obtained by adding successively carbazole-3-diazonium chloride and sodium hydroxide to a solution of β-naphthylamine hydrochloride (Found: N = 16.78.  $C_{22}H_{16}N_4$  requires N = 16.67 per cent.). Concentrated sulphuric acid developed a deep blue coloration, becoming violet on dilution.

*Carbazole-3-diazocyanide*,  $NH \cdot C_{12}H_7 \cdot N_2 \cdot CN$ , was obtained by double decomposition from carbazole-3-diazonium chloride in either alkaline or acid solution. Aqueous potassium cyanide was added to a dilute solution of the diazonium chloride, rendered alkaline with sodium carbonate. A dark brownish-red precipitate was deposited, changing quickly to brilliant red. Crystallisation of the product from 50 per cent. alcohol yielded small, brick-red needles darkening on heating and decomposing at 155–160°.

On adding the aqueous cyanide to a solution of diazonium chloride containing excess of hydrochloric acid, a brick-red precipitate was obtained which, when crystallised from dilute alcohol, also separated in brick-red needles identical with the preceding preparation (Found: N = 25.51.  $C_{13}H_8N_4$  requires N = 25.48 per cent.). This diazocyanide condensed very slowly with alkaline β-naphthol, several hours elapsing before the reaction was completed. This slow rate of coupling suggested the *anti*-form of the cyanide. The compound was insoluble in the organic media and slowly became brown on exposure to light.

*Carbazole-3-diazonium nitroprusside*,  $(NH \cdot C_{12}H_7 \cdot N_2)_2 Fe(CN)_5 NO$ , an amorphous, light yellow precipitate produced by double decomposition and becoming brown on exposure (Found: N = 28.08; Fe = 9.21.  $C_{22}H_{16}ON_{12}Fe$  requires N = 27.82; Fe = 9.27 per cent.). This compound, when heated rapidly, became green at 150° and decomposed explosively at 160°.

*3-Triazocarbazole* (*Carbazole-3-azoimide*. Formula IV).—On mixing aqueous solutions of sodium azide and carbazole-3-diazonium chloride, the yellow colour of the latter salt gradually faded, nitrogen was evolved, and a white precipitate of the triazo-compound was obtained in quantitative yield. This product was fairly soluble in the ordinary organic solvents and crystallised readily from ether, alcohol, or ligroin, separating in lustrous, colourless plates melting with violent evolution of gas at 176–177° (Found: N = 27.68.  $C_{12}H_8N_4$  requires N = 26.92 per cent.). 3-Triazocarbazole became brown on exposure to light and decomposed with considerable violence when dropped into concentrated sulphuric acid, the

mixture becoming greenish-blue. Attempts made to moderate this reaction by using dilute sulphuric acid with or without a catalyst (copper powder) led to the production of an ill-defined blue product mixed with a primary amine obtained only in small proportion.

*Ethyl Carbazole-3-azoacetoacetate*,  $\text{HN}:\text{C}_{12}\text{H}_7\cdot\text{N}_2\cdot\text{C}\begin{smallmatrix} \text{C}(\text{OH})\cdot\text{CH}_3 \\ \text{CO}_2\cdot\text{C}_2\text{H}_5 \end{smallmatrix}$ ,

obtained by adding alcoholic ethyl acetoacetate and sodium acetate in succession to carbazole-3-diazonium chloride in aqueous solution, crystallised from alcohol in golden-yellow, prismatic needles melting at  $193^\circ$  (Found:  $\text{N} = 13.27$ .  $\text{C}_{18}\text{H}_{17}\text{O}_3\text{N}_3$  requires  $\text{N} = 13.00$  per cent.).

*N-Ethylcarbazole-3-diazonium chloride* (Formula VI).—The starting material, *N*-ethylcarbazole, obtained from the Gas, Light, and Coke Company, was nitrated by a modification of the process outlined in D.R.-P. 294016 (1913). Fifty grams of ethylcarbazole, dissolved in 125 c.c. of benzene, were added slowly to 60 c.c. of nitric acid ( $\text{HNO}_3 = 43.4$  per cent.) cooled to  $0^\circ$ , and stirred mechanically. The greenish-yellow 3-nitro-*N*-ethylcarbazole, which gradually separated until the mixture became solid, crystallised from alcohol in bright yellow needles melting at  $126^\circ$  (compare D.R.-P. 259504, *Frdl.* XI. 172).

3-Nitro-*N*-ethylcarbazole (20 grams) was refluxed for one hour with 30 grams of granulated tin, 100 c.c. of concentrated hydrochloric acid, and 35 c.c. of glacial acetic acid. The light brown solution yielded on cooling 34 grams of brownish-white 3-amino-*N*-ethylcarbazole stannichloride, and after removing the tin with hydrogen sulphide, colourless needles of the hydrochloride were obtained on concentrating the filtrate, the average yield being 75 per cent. (Found:  $\text{N} = 11.11$ .  $\text{C}_{14}\text{H}_{15}\text{N}_2\text{Cl}$  requires  $\text{N} = 11.36$  per cent.). This hydrochloride resembled 3-aminocarbazole hydrochloride in yielding so stable a diazonium salt that diazotisation could be effected at  $15\text{--}20^\circ$ : 5 grams of 3-amino-*N*-ethylcarbazole hydrochloride, 6 c.c. of concentrated hydrochloric acid, 15 c.c. of water, 2 grams of sodium nitrite in 10 c.c. of water. The dark brown solution, filtered from a small amount of green, slimy product, was cooled in ice, when the diazonium salt separated in golden-yellow needles, recrystallised from water at  $18^\circ$  on cooling the solution to  $-3^\circ$  (Found:  $\text{N} = 14.12$ ;  $\text{Cl} = 12.09$ ;  $\text{H}_2\text{O} = 12.28$ .  $\text{C}_{14}\text{H}_{12}\text{N}_3\text{Cl}\cdot 2\text{H}_2\text{O}$  requires  $\text{N} = 14.31$ ;  $\text{Cl} = 12.10$ ;  $\text{H}_2\text{O} = 12.27$  per cent.). The hydrated chloride liquefied partly, changing from golden-yellow to canary-yellow; at  $149\text{--}150^\circ$ , it turned grey and melted completely with decomposition; it lost its water in a vacuum over sulphuric acid and then decomposed at  $149\text{--}150^\circ$  (Found:

N = 16.10; Cl = 13.86, 13.75.  $C_{14}H_{12}N_3Cl$  requires N = 16.31; Cl = 13.75 per cent.). The anhydrous chloride was also obtained in canary-yellow needles by adding ether to an alcoholic solution of the hydrated salt. When left in the air, the water of crystallisation was recovered quantitatively. The action of light on *N*-ethylcarbazole-3-diazonium chloride was inappreciable, in which respect this salt differed considerably from the photochemical carbazole-3-diazonium chloride.

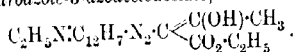
3-Triazo-*N*-ethylcarbazole, obtained by double decomposition from the chloride and sodium azide in aqueous solution, was oily and was not further examined.

*N*-Ethylcarbazole-3-diazonium aurichloride,  $C_2H_5N(C_{12}H_7N_2)_2AuCl_4$ , a light yellow compound, produced by double decomposition, contained Au = 35.37.  $C_{14}H_{12}N_3Cl_4Au$  requires Au = 35.12 per cent.

*N*-Ethylcarbazole-3-diazonium dichromate,  $(C_2H_5N(C_{12}H_7N_2)_2)_2Cr_2O_7$ , a comparatively stable salt separating in bright yellow, acicular prisms from aqueous solution of the chloride and an alkali dichromate, was more soluble in hot water (Found: Cr = 15.90.  $C_{28}H_{24}O_7N_6Cr_2$  requires Cr = 15.76 per cent.).

*N*-Ethylcarbazole-3-diazonium cyanide, a bright red compound separating from alcohol in needles, prepared by double decomposition in acid or alkaline solutions, coupled very slowly with alkaline  $\beta$ -naphthol and decomposed indefinitely at 148–155° (Found: N = 22.53.  $C_{15}H_{12}N_4$  requires N = 22.58 per cent.). The corresponding nitroprusside,  $[Fe(CN)_5NO] (N_2C_{12}H_7N(C_2H_5))_2$ , separated in bright yellow, microscopic needles (Found: N = 25.56.  $C_{33}H_{24}ON_{12}Fe$  requires N = 25.46 per cent.).

*Ethyl N*-ethylcarbazole-3-azoacetate,



—An alcoholic solution of ethyl acetoacetate and crystalline sodium acetate were added to aqueous *N*-ethylcarbazole-3-diazonium chloride, and the azo-condensation product, which separated as an oily mass, was obtained solid from ether and recrystallised from alcohol in golden-yellow needles melting at 125° (Found: N = 12.06.  $C_{20}H_{21}O_3N_3$  requires N = 11.96 per cent.).

*Action of Aqueous Ammonia on N*-Ethylcarbazole-3-diazonium Chloride.—So far the behaviour of *N*-ethylcarbazole-3-diazonium chloride closely resembled that of carbazole-3-diazonium chloride, but the reactions of these salts with ammonia were quite different. On adding 10 c.c. of concentrated ammonia to 0.5 gram of anhydrous *N*-ethylcarbazole-3-diazonium chloride in 30 c.c. of water at 0°, the solution became reddish-brown and a brown, amorphous solid

slowly separated with evolution of gas. There was no appearance of a crystalline product comparable with that from carbazole-3-diazonium chloride and ammonia. The experiment was repeated in a volumeter, when the loss of nitrogen was 5.10 per cent.; for half the diazo-nitrogen this percentage should be 5.44. The solid product, although insoluble in water, dissolved readily in benzene, being precipitated therefrom by light petroleum as a light brown, microcrystalline substance charring at 150—155° (Found:  $N = 12.76$ .  $C_{28}H_{24}ON_4$  requires  $N = 12.96$  per cent.), a result corresponding with the composition of an external diazo-oxide. When treated with concentrated hydrochloric acid, this substance was decomposed into a greenish-blue, indefinite product and *N*-ethylcarbazole-3-diazonium chloride, the latter being identified by its bright yellow colour and power of coupling with alkaline  $\beta$ -naphthol to a reddish-violet azo-compound.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

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### CCCXXVI.—*The Oxidation of Sabinene with Chromyl Chloride.*

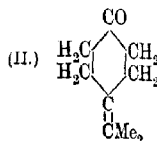
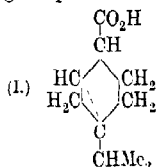
by GEORGE GERALD HENDERSON, JOHN MCGREGOR ROBERTSON,  
and DAVID CHRISTIE BROWN.

PREVIOUS investigations have shown that a number of the terpenes, both monocyclic and dicyclic, unite additively with chromyl chloride to form solid compounds of the formula  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ , which, when decomposed by water, yield mixtures of aldehydes and ketones derived from the corresponding hydrocarbons (Bredt and Jagelki, *Annalen*, 1900, **310**, 112; Henderson and others, *T.*, 1903, **83**, 1299; 1908, **93**, 288; 1911, **99**, 1887). It has now been found that in this respect sabinene resembles other dicyclic terpenes. When a dilute solution of chromyl chloride in carbon disulphide is slowly added to a similar solution of sabinene, care being taken to prevent rise of temperature, a solid separates. This compound is readily decomposed by water, with formation of an insoluble liquid product together with a certain quantity of resinous matter. The principal constituents of the liquid, apart from some indefinite

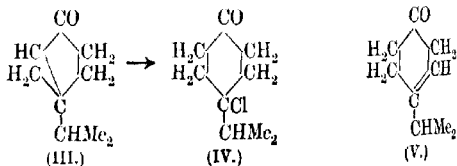


resinous materials, are a saturated *aldehyde*,  $C_9H_{15}\cdot CHO$ , and an unsaturated ketone,  $C_9H_{14}O$ , which are present in approximately equal proportions. In addition, a small quantity of an isomeric ketone was separated in the form of its semicarbazone.

The aldehyde, which is a viscous liquid, undergoes spontaneous oxidation on exposure to air. The crystalline *acid*,  $C_9H_{15}\cdot CO_2H$ , thus produced melts at  $175^\circ$ ; it is also obtained when the aldehyde is heated with dilute nitric acid. As the acid is prepared from sabinene by a method similar to that by which camphene is converted into camphenilanic acid, it may be named sabinenilanic acid. Its constitution has not been elucidated as yet, but if it be assumed that the structure of the sabinene nucleus remains unchanged during the process of oxidation, the formula will be (I).



The two ketones were separated by taking advantage of the difference in solubility of their semicarbazones, that of the chief constituent being very sparingly soluble and the other readily soluble in cold alcohol. After several crystallisations, the former semicarbazone showed a constant melting point of  $205^\circ$ . The ketone,  $C_9H_{14}O$ , liberated from it is a colourless liquid of pleasant odour, which boils at  $220^\circ$  and behaves as an unsaturated compound towards bromine and potassium permanganate. Taking into account the properties of the ketone as well as those of its semicarbazone, there can be little doubt that it is 4-isopropylidene cyclohexanone (II). This ketone was obtained by Perkin (I., 1907, 91, 1736) as a product of the hydrolysis of ethyl 4-isopropylidene- $\delta$ cyclohexanone-2-carboxylate, and also by Wallach (*Annalen*, 1908, 359, 265) on heating with dimethylaniline the compound (IV) which he had prepared by the action of hydrogen chloride on sabinone (III). The melting point of the semicarbazone of our ketone is, however, somewhat higher than that ( $201^\circ$ ) quoted by these observers.



On reduction with sodium and alcohol, the ketone is converted into the secondary alcohol, 4-isopropylidenecyclohexanol,  $C_8H_{14}>CH\cdot OH$ , a liquid with a pleasant odour which boils at  $134^\circ/40$  mm. Its *p*-nitrobenzoate is a colourless, crystalline solid, m. p.  $63^\circ$ .

After repeated crystallisations, the melting point of the semicarbazone of the ketone present in small quantity in the original oxidation product was found to be  $168\text{--}169^\circ$ , whilst Wallach (*loc. cit.*) gives as  $169\text{--}170^\circ$  the melting point of the semicarbazone of 4-isopropyl- $\Delta^2$ -cyclohexenone (V). This ketone he obtained, together with the isomeric  $\Delta^2$ -compound as principal product, on heating sabina ketone with 20 per cent. sulphuric acid. The quantity of the semicarbazone of m. p.  $169^\circ$  in our hands was so small that it was not possible to separate and identify the ketone.

It might have been anticipated that sabina ketone would be one of the products of the action of chromyl chloride on sabinene and it is at least possible that this was actually the case, and that the sabina ketone originally formed was caused to undergo intramolecular rearrangement under the influence of the hydrochloric acid which is always liberated along with chromium chloride and a little chromic acid when the additive products,  $C_{10}H_{16}\cdot 2CrO_2Cl_2$ , are decomposed by water. If that had been the case, however, one would have expected, in view of Wallach's results, to find 4-isopropyl- $\Delta^2$ -cyclohexenone in our product, whereas none of this compound could be detected.

## EXPERIMENTAL.

### *Separation and Oxidation of Sabinene.*

Sabinene was separated from oil of savin as follows. The oil was distilled in a current of steam for about half an hour, and the oily distillate collected and treated under reflux for some time with sufficient alcoholic sodium hydroxide to hydrolyse the sabinol esters which it contained. After passing in carbon dioxide to neutralise any free alkali, the mixture was distilled in steam, and the distillate collected in two approximately equal fractions. The first of these, which contained practically all the sabinene, was extracted with light petroleum, the extract dried over anhydrous sodium sulphate, the solvent removed, and the residual liquid distilled in a current of dry carbon dioxide. The yield of sabinene (b. p.  $163\text{--}165^\circ$ ) obtained was nearly 19 per cent. of the weight of the oil of savin.

A 10 per cent. solution of 100 grams (rather more than 2 mols.) of chromyl chloride in carbon disulphide was added, in small quantities at a time and with constant agitation, to a similar solution of 40 grams (1 mol.) of sabinene, both solutions being well cooled with ice-water. During this part of the process, any failure to

keep the solution cool results in much loss by resinification of the sabinene. A precipitate of the solid compound began to separate at once, and was left to settle for a day or two. The liquid was then decanted, and the thin, pasty mixture of the solid compound and carbon disulphide poured, in small quantities at a time, into ice-cold water, with vigorous agitation after each addition. The quantity of carbon disulphide present in the mixture was sufficient to extract most of the oxidation product from the water, and the last traces were recovered by successive extractions with ether and with light petroleum. The solutions were washed with water and dried over anhydrous sodium sulphate, and the solvents removed by distillation. As the residual oxidation product contained a considerable proportion of resinous substances, it was further purified by distillation in steam, an approximately 50 per cent. yield being obtained.

The solid additive compound,  $C_{10}H_{16} \cdot 2CrO_2Cl_2$ , is very similar to those obtained from other terpenes. When dry, it is a grey powder, which quickly begins to undergo decomposition when exposed to moist air, and which reacts vigorously with water.

#### *Separation and Oxidation of Sabinenilanaldehyde.*

The oxidation product, after steam distillation, was mixed with excess of a freshly prepared saturated solution of sodium hydrogen sulphite, and shaken at intervals for several days. The bisulphite compound, which separated slowly in the form of a colourless, finely crystalline solid, was collected and washed with alcohol and with ether. The residual oily liquid recovered from the filtrate and washings was again shaken with sodium hydrogen sulphite, and the process repeated until no further separation of crystals took place. The bisulphite compound was heated with excess of aqueous sodium carbonate, and the liberated aldehyde distilled off in a current of steam, separated from the distillate by means of ether, and purified by distillation.

*Sabinenilanaldehyde*,  $C_9H_{15} \cdot CHO$ , is an almost colourless, viscous liquid, which boils at  $215-217^\circ$ , and has the strong, peculiar odour characteristic of such terpene aldehydes. It dissolves easily in the usual organic solvents, and is oxidised to the corresponding acid when exposed to air. The *semicarbazone* of the aldehyde, prepared in the usual manner, separates from methyl alcohol, in which it is freely soluble, in colourless crystals, m. p.  $145-146^\circ$  (Found:  $N = 20.0$ .  $C_{10}H_{16}O$  requires  $N = 20.1$  per cent.).

*Sabinenilanic acid*,  $C_9H_{15} \cdot CO_2H$ , was prepared by spontaneous oxidation of the aldehyde, and also by heating it with dilute nitric acid. It was purified by crystallisation from benzene, from which it separates in small, colourless prisms, m. p.  $175-176^\circ$ . It is

very readily soluble in alcohol or ether, and sparingly soluble in water or cold benzene. Towards bromine or potassium permanganate, it behaves as a saturated compound. The *sodium*, *calcium*, and *barium* salts are readily soluble in water, the *silver* salt almost insoluble (Found: C = 71.3; H = 9.7.  $C_{10}H_{16}O_2$  requires C = 71.4; H = 9.5 per cent.).

*Separation and Reduction of 4-isopropylidenecyclohexanone.*

The mixed ketones which remained after removal of the aldehyde from the original oxidation product were converted into semicarbazones in the usual manner. The mixture of semicarbazones was dissolved in boiling alcohol and on cooling the bulk crystallised, but a small portion remained in solution and was precipitated by addition of water after removal of the crop of crystals. By repetition of this process, we obtained a semicarbazone which melted sharply at  $205^\circ$ , and a small quantity of a second semicarbazone with a melting point of  $168-169^\circ$ . The ketone, 4-isopropylidenecyclohexanone,  $C_9H_{14}O$ , was prepared by decomposing the semicarbazone of m. p.  $205^\circ$  with the calculated quantity of oxalic acid, distilling the mixture in a current of steam, and extracting the ketone from the distillate with ether. It is a colourless liquid of a pleasant odour which distils at  $220^\circ$  without decomposition, and as an unsaturated compound at once reacts with bromine and with potassium permanganate. It is almost insoluble in water, and readily soluble in alcohol or ether. Its composition was determined by analysis of the semicarbazone (Found: C = 61.9; H = 8.7; N = 21.7. Calc., C = 61.5; H = 8.8; N = 21.5 per cent.).

The corresponding *alcohol*, 4-isopropylidenecyclohexanol,  $C_9H_{14}>CH-OH$ , was prepared by addition of sodium in excess to a methyl-alcoholic solution of the ketone, and subsequent treatment with water, extraction with ether, and distillation of the crude product under diminished pressure. The alcohol was thus obtained as a colourless, viscous liquid with an odour somewhat like that of menthol. It boils at  $134^\circ/40$  mm. and is sparingly soluble in water, but dissolves easily in alcohol or ether. When treated, in pyridine solution, with *p*-nitrobenzoyl chloride, it yields a *p*-nitrobenzoate, which crystallises from alcohol in small, colourless prisms, m. p.  $63^\circ$ .

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us (J. M. R.) to take part in this work, and to the Carnegie Trust for a grant which defrayed part of the expense.

CCCXXVII.—*Resorcinolphenylsuccinein.*

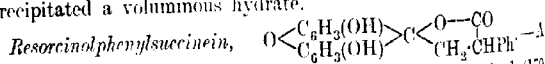
By ARTHUR LAPWORTH and JOHN ALEXANDER MCRAE.

THE improvements in the modes of preparing succinic acids containing aromatic substituents, described by the authors in another communication (this vol., p. 1699), make it possible to obtain many of these compounds cheaply and if necessary in large quantity. It therefore seemed worth while to examine their application for the preparation of colouring matters, where there is a very wide field to be explored. The time which it was necessary to devote to the study of other aspects of the syntheses of the succinic acids deflected attention from what was the original line of work; the preparation and characterisation of resorcinolphenylsuccinein and its tetrabromo-derivative were completed, however, and as the authors are no longer able to work in collaboration, the results are here recorded.

The methods described in the literature for the preparation of resorcinolsuccinein by the condensation of succinic anhydride and resorcinol (Nencki and Sieber, *J. pr. Chem.*, 1881, [ii], 23, 152), and of fluorescein, do not seem at first sight to offer any great difficulty; but a closer examination shows that these substances are formed along with by-products from which sometimes it is not easy to obtain the pure compound. Considerable doubt seems to be associated with the characterisation of fluorescein, for H. v. Liebig (*J. pr. Chem.*, 1912, [ii], 85, 97, 241) claims to have isolated five different modifications of this substance.

It was found a relatively simple matter to effect the condensation of phenylsuccinic acid with resorcinol, but it was with considerable difficulty that a pure crystalline specimen of the product was isolated. Phenylsuccinein appears to give two bromo-derivatives, one colourless and crystalline, the other red and amorphous.

The colourless form dissolves in dilute alkali to give an intensely red solution which yields on acidification an amorphous, red substance. The relation of these substances was not investigated in detail, but it may be noted that Pratt, Hutchinson, and Harvey (*J. Amer. Chem. Soc.*, 1919, 41, 1293) obtained tetrabromococoin by the bromination of tetrabromofluorescein as a faintly pink substance giving intensely coloured solutions in alkali from which acids precipitated a voluminous hydrate.



mixture of phenylsuccinic acid (146 grams) and resorcinol (170 grams) was heated in an oil-bath at 135° and 19.5 grams of freshly fused and finely powdered zinc chloride, prepared according to

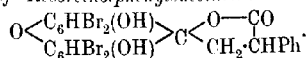
Copisarow (T., 1920, **117**, 209), were stirred in. The mixture was heated for seven hours at 135–145°, by which time the contents of the flask had become solid. The melt was dissolved in very dilute caustic soda (about 3 per cent.) and then acidified slowly with dilute hydrochloric acid, avoiding any temporary local excess of acid, which caused the precipitate to "ball" together. The brown, amorphous precipitate after drying was boiled with alcohol, leaving a residue of 9 grams, which was dissolved in hot phenol and filtered while hot from a small amount of insoluble material; on the addition of alcohol to the filtrate a yellow, semi-crystalline substance was precipitated. This was collected, washed well with alcohol, and heated under reduced pressure at 100° until the odour of phenol disappeared. It melted and decomposed at 249° (Found: C = 74.0; H = 4.4.  $C_{22}H_{16}O_5$  requires C = 73.33; H = 4.44 per cent.).

*Resorcinolphenylsuccinein* is an orange, semi-crystalline substance very slightly soluble in water and sparingly soluble in alcohol, giving a yellow solution with green fluorescence. The dried substance dissolves slowly in ether, although the freshly precipitated material dissolves readily. It is readily soluble in acetone or acetic acid, very slightly soluble in benzene, and moderately soluble in hot phenol. On boiling with benzene, it becomes dark red.

It dissolves in concentrated sulphuric acid forming a deep yellow solution with a bluish-green fluorescence; with dilute caustic soda it gives a red solution which on dilution has an intense green fluorescence, and a direct comparison showed that the intensity was of the same order as with fluorescein in similar circumstances.

A number of other condensing agents were tried for the preparation of this succinein, including concentrated sulphuric acid and phosphoryl chloride. Some experiments with stannic chloride, made almost at the end of the work on the phenylsuccinein, seemed to show that it could replace zinc chloride with advantage. In another experiment, the method used by Friedl, Weizmann, and Wyler (T., 1907, **81**, 1585) in the making of the fluorescein of 4-hydroxyphthalic acid was tried, with favourable results; the method as applied to the present case consisted in heating phenylsuccinic acid and resorcinol with a large excess of a concentrated solution of zinc chloride.

*Bromination of Resorcinolphenylsuccinein. Phenylsuccinyleosin,*



—Three grams of resorcinolphenylsuccinein were suspended in 20 c.c. of alcohol and 6 grams of bromine (slightly more than 4 mols.) were dropped in, the succinein going into solution as the reaction took place. The solvent was allowed to evaporate and the residue

rubbed up with benzene, which dissolved the greater part but left a faintly coloured residue; this, when recrystallised three times from alcohol, gave an almost colourless substance softening at  $283^{\circ}$  and melting at  $295^{\circ}$ . It became slightly pink on standing in the vacuum desiccator (Found: by Robertson's method, Br = 46.46,  $C_{22}H_{12}O_5Br_4$  requires Br = 47.33 per cent.).

The substance dissolves in alkali to give an intensely purple-red solution, which on standing deposits an amorphous, brown precipitate which no longer dissolves in alkali. If the alkaline solution is acidified quickly, a red, amorphous precipitate is obtained which can again be dissolved in alkali to give a red solution but not of the original intensity.

A crystalline compound was not isolated from the benzene extract of the bromination product. Only a red, amorphous substance could be obtained.

The authors' thanks are due to the Canadian Honorary Advisory Council for Scientific and Industrial Research for the grant of a fellowship to one of us (J. A. M.) which enabled him to take part in this work.

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(Received, November 3rd, 1932.)

### CCCXXVIII.—*The Reactivity of Methyl Groups in Heterocyclic Bases.*

By WILLIAM HOBSON MILLS and JAMES LEONARD BRIERLEY SMITH.

IN its characteristic reactivity, the 2-methyl group in quinaldine,  $\alpha$ -picoline, and similar heterocyclic bases corresponds in many respects with the methyl group in such compounds as the methyl ketones or nitromethane, or with the methylene group in phenylacetonitrile.

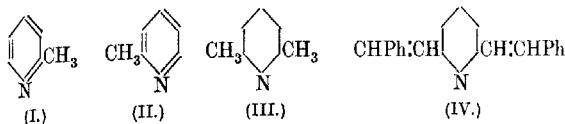
In these substances, it has long been recognised (for example, Henrich, *Ber.*, 1899, **32**, 688) that a marked similarity in constitution exists; the methyl or methylene group is in each case attached to a multivalent element, Y, which is in turn doubly (or trebly) linked to an element of strongly "negative" character, Z, according to a scheme such as  $-(CH_2 \cdot Y \cdot Z)$ .

It is therefore probable that, as was suggested by Henrich\*

\* Plancher (*Gazzetta*, 1898, **28**, ii, 417) made a similar suggestion to account for the reactivity of the 2-methyl group in 2-methyl-3:3-diethylindolenine.

(compare Vorländer, *Ber.*, 1902, **35**, 4145), the 2-methyl group in the bases of the pyridine and quinoline series owes its reactivity to its being associated, as represented in the Körner-Dewar formula for pyridine, with a  $\text{-}\dot{\text{C}}\text{:N-}$  group, the effect of the  $\text{-}\dot{\text{C}}\text{:N-}$  on the methyl group in the grouping  $\text{CH}_3\text{:}\dot{\text{C}}\text{:N-}$  corresponding with that of the carbonyl group in the grouping  $\text{CH}_3\text{:}\dot{\text{C}}\text{:O}$  of the methyl ketones.

If this is true, the possibility of the existence of two chemically distinct forms of  $\alpha$ -picoline is indicated, one (I) with a reactive, the other (II) with a non-reactive methyl group. It is scarcely to be

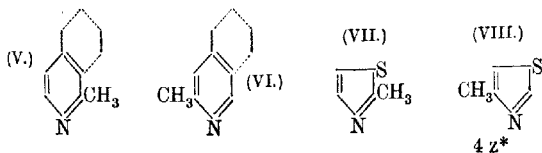


expected that these two forms could be obtained each apart from the other on account of the mobility of the system of linkages existing in the pyridine ring; for example, 2:6-dimethylpyridine (III) gives with benzaldehyde and zinc chloride a dibenzylidene derivative (IV) (Schuster, *Ber.*, 1892, **25**, 2398).

If, however, by some means, the mobility of the linkings in the pyridine ring could be diminished, it might be possible to demonstrate a difference of reactivity of the methyl groups attached to the carbon atoms on either side of the nitrogen atom.

There are two obvious methods by which the mobility of the linkages in a ring of this kind can be limited. The first consists in the fusion of the pyridine ring with a benzene ring so as to produce an *isoquinoline* nucleus. The tendency of each of the two six-membered rings to maintain its aromatic character should then fix the linkings in the resulting *isoquinoline* nucleus in positions corresponding with those assumed in Erlenmeyer's naphthalene formula. Marckwald (*Annalen*, 1893, **274**, 331; 1894, **279**, 1) has shown that much experimental evidence exists in favour of this view.

The two isomeric  $\alpha$ -picolines fused thus with a benzene ring give 1-methyl*isoquinoline* (V) and 3-methyl*isoquinoline* (VI), respectively. The former compound should contain a reactive, the latter a non-reactive, methyl group.



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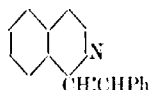


The second method of fixing the linkages depends on the possibility of replacing a  $-C_2H_2-$  group in the pyridine ring by an atom of sulphur. This replacement gives, instead of pyridine bases, bases of the thiazole series, and the resemblance in physical and chemical properties between the compounds of the two series, which Hantzsch has described (*Annalen*, 1889, **250**, 258), is even more striking than that between benzene and thiophen. In place of the two forms of  $\alpha$ -picoline we then have 2-methylthiazole (VII) and 4-methylthiazole (VIII), and according to the foregoing considerations the former should contain a reactive, the latter a non-reactive, methyl group.

Investigation of these *isoquinoline* and thiazole derivatives has shown that in fact the properties of a methyl group adjacent to the cyclic nitrogen atom in bases of this type differ in the most marked manner according to the side of the nitrogen atom on which the group is situated.

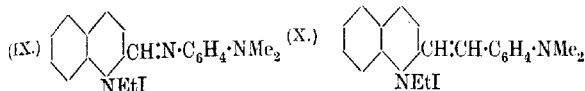
The isomeric 1- and 3-methyl*isoquinolines* were first investigated. Their behaviour towards benzaldehyde was compared and was found to stand in sharp contrast.

When 1-methyl*isoquinoline* was treated with benzaldehyde at  $100^\circ$  in presence of a small quantity of zinc chloride, condensation was found to take place readily; water was seen to separate, and the condensation product, 1-styryl*isoquinoline*, crystallised on cooling.



When 3-methyl*isoquinoline*, on the other hand, was heated with benzaldehyde and zinc chloride under corresponding conditions, no condensation took place even after prolonged heating; there was no separation of water, and the base and the benzaldehyde could both be recovered unchanged.

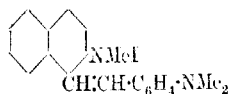
The reactivity of the methiodides of the two bases was then compared. The reactive character of the 2-methyl group in bases like  $\alpha$ -picoline and quinaldine becomes greatly enhanced when the bases are converted into their quaternary salts. For example,  $\alpha$ -picoline and quinaldine apparently cannot be made to condense with nitrosodimethylaniline. The alkylidides of these bases, however, condense with nitrosodimethylaniline with very great ease in alcoholic solution in presence of piperidine to give azomethine derivatives, quinaldine ethiodide for instance giving the compound IX (Kaufmann, *Ber.*, 1912, **45**, 1736):



Again, quinaldine can be made to condense with *p*-dimethylaminobenzaldehyde, as Mr. E. S. Dewing and one of us have found, by heating the two substances together for some hours at 100° with zinc chloride; but quinaldine ethiodide, in presence of a small quantity of piperidine, condenses with this aldehyde even in dilute alcoholic solution, giving *p*-dimethylaminostyryl derivatives, such as the compound (X) obtained from quinaldine ethiodide (König, *J. pr. Chem.*, 1912, [ii], 86, 172; 1921, [ii], 102, 63; Barbier, *Bull. Soc. chim.*, 1920, [iv], 27, 427; Pope and Mills, this vol., p. 946).

On account of the readiness with which these condensations take place and the intense colour of the products, they provide an exceedingly delicate test for the reactivity of a methyl group in bases of the type under consideration. On investigating the methiodides of 1- and 3-methylisoquinoline in this manner, a difference in reactivity was observed which corresponded exactly with that shown by the free bases.

When 1-methylisoquinoline was heated in alcoholic solution with *p*-dimethylaminobenzaldehyde in presence of a small quantity of piperidine, a deep red colour was very rapidly produced and the condensation product to which it was due, 1-*p*-dimethylaminostyryl-isoquinoline methiodide,



was easily isolated in crystalline form.

When, however, 3-methylisoquinoline methiodide was treated in the same way, no trace of colour characteristic of a *p*-dimethylaminostyryl dyestuff appeared and no other evidence of the occurrence of condensation could be obtained.

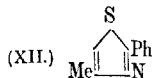
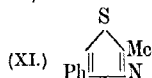
Similarly, a hot alcoholic solution of 1-methylisoquinoline methiodide and nitrosodimethylaniline, on addition of a few drops of piperidine, at once became deep purple, evidently on account of the formation of a dimethylaminoazomethine derivative, whilst in the corresponding mixture in which the 1-methyl methiodide was replaced by the 3-methyl isomeride, there was no development of colour.

Further, it appears that 1-methylisoquinoline methiodide can undergo a cyanine condensation with quinoline alkylidides, but

that 3-methylisoquinoline methiodide is unable to take part in such a reaction; for on heating the latter methiodide with an alcoholic solution of quinoline methiodide and sodium hydroxide no colour appeared, but with the former an intense red colour was quickly developed and the solution then showed a double absorption band in the green similar to that which characterises the isocyanines.

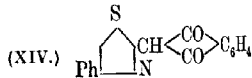
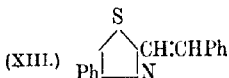
After the great contrast in the reactivity of methyl groups in the 1- and 3-positions in isoquinoline and its quaternary salts had thus been demonstrated, we proceeded to examine the methyl derivatives of the bases of the thiazole series in a similar manner.

The simple methylthiazoles are somewhat difficult to prepare. Our experiments were therefore carried out with the two isomeric compounds, 4-phenyl-2-methylthiazole (XI) and 2-phenyl-4-methylthiazole (XII), which are readily obtainable by methods described by Hantzsch (*Annalen*, 1889, 250, 269) and Hubacher (*Annalen*, 1890, 259, 236):



The methyl groups in these compounds showed a difference in reactivity which was entirely comparable with that of those in the two methylisoquinolines.

The methyl group in 4-phenyl-2-methylthiazole was even more reactive than that in 1-methylisoquinoline. The free base entered into condensation with benzaldehyde very readily to give 4-phenyl-2-styrylthiazole (XIII); it also condensed with phthalic anhydride to give the thiazole analogue of quinophthalone (XIV).



The reactivity of the methiodide was still more pronounced. With the greatest facility it gave a *p*-dimethylaminostyryl derivative with *p*-dimethylaminobenzaldehyde, an azomethine derivative with nitrosodimethylaniline, and a dye of the cyanine type with quinoline methiodide and alkali.

In the isomeric base, 2-phenyl-4-methylthiazole (XII), on the other hand, the methyl group, at least so far as reactions of the type of the foregoing are concerned, was found to be completely non-reactive. The free base could not be made to condense with benzaldehyde, and the methiodide appeared to be wholly indifferent towards *p*-dimethylaminobenzaldehyde or nitrosodimethylaniline.

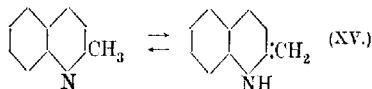
and to be incapable of forming a cyanine dye with quinoline methiodide and alkali.

It is thus perfectly clear that there is a very definite difference in the reactivity of a substituent methyl group adjacent to the nitrogen atom in *isoquinoline* and thiazole bases according as it is situated on one side or the other of the nitrogen.

This would appear to provide evidence of some corresponding difference between the linkings by which the nitrogen atom in *isoquinoline* and thiazole nuclei is attached to the carbon atom on either side of it and thus to support that view of the constitution of the nuclei of these heterocyclic bases, which was used as the basis of the considerations at the beginning of this paper, according to which the atoms are regarded as alternately singly and doubly linked, as in Kekulé's formula for benzene.

It is nevertheless desirable to consider the facts more closely. There is an evident similarity, as has already been stated, between the types of reaction of which the methyl groups in these nitrogenous heterocyclic bases are capable and those which are characteristic of the methyl group in the methyl ketones. It appears, however, to follow, from the work of Lapworth on acetone (T., 1904, 85, 30) and that of Dimroth (*Ber.*, 1907, 40, 2404) and K. H. Meyer (*Annalen*, 1911, 379, 59; 380, 212, etc.) on the relative activity of keto- and enol-desmotropes, that the distinctive reactivity of the methyl in compounds containing the grouping  $\text{CH}_3\text{CO}-$  is dependent on their capability of passing over in a greater or less degree into enolic modifications. It is therefore exceedingly probable that the capacity of the methyl group as such for direct condensation is comparatively slight.

If this is so, then the marked power which quinaldine, for example, possesses of condensing with aldehydes and similar substances must be due to the presence, under the conditions of the reaction, of a small quantity of a reactive tautomeride with which it exists in equilibrium. Such a tautomeride could scarcely be other than the substance XV, the constitution of which corresponds closely

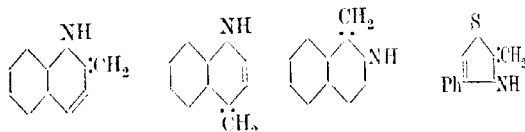


with that of the enolic modifications of methyl ketones. The reactivity assigned to this substance is in harmony with the work of K. H. Meyer (*Ber.*, 1921, 54, [B], 2265, 2268), who has given reasons for attributing great activity to the groupings  $\text{NH}_2\text{C}\cdot\text{CH}_3$  and  $\text{NMe}_2\text{C}\cdot\text{CH}_3$ . There is also evidence, from analogy to show that there is nothing improbable in the assumption of the limited form-

ation of such a compound from quinaldine, for the occurrence of somewhat similar changes in pyridine and quinoline derivatives is clearly indicated (for example, Marekwald and Meyer, *Ber.*, 1900, 33, 1885; Fargher and Furness, *T.*, 1915, 107, 688; compare Tschitschibabin and R. and A. Konowalowa, *Ber.*, 1921, 54, [4], 814), and substitution derivatives of this and analogous compounds exist (for example, Brunner, *Ber.*, 1898, 31, 1947; Decker and Klauser, *Ber.*, 1904, 37, 528; Hamilton and Robinson, *T.*, 1916, 109, 1035; Mills, this vol., p. 457).\*

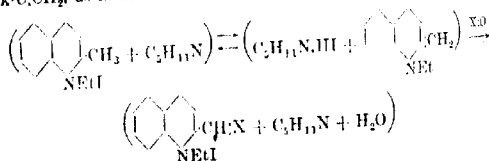
It is therefore possible to consider the difference in reactivity shown by a methyl group in these heterocyclic bases according as it lies on one side or the other of the nitrogen atom not only from the point of view of the nitrogen-carbon linkages, but also from the different but closely related aspect of tautomeric change. The contrast in properties observed in the pairs of isomerides studied may be regarded as indicating that passage into a reactive form is possible when the methyl group is in the one position, but not when it is in the other.

On this view, the reactivity of the methyl groups in quinaldine, lepidine, 1-methylisoquinoline, and 4-phenyl-2-methylthiazole is dependent on a power possessed by these bases of passing over to some extent into forms of the constitutions:

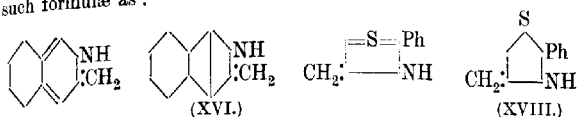


\* From this point of view, the reactivity of the methyl group in the quaternary salts of quinaldine and similar bases becomes more readily intelligible. For the various condensations of these substances with compounds of the type X:O (aldehydes, nitroso-compounds, etc.) are brought about in presence of strong bases, such as piperidine—that is to say, under conditions under which a certain amount of the quaternary salt must be converted by removal of the acid into the N-alkyl derivative of that compound to which the reactivity of the free base is ascribed.

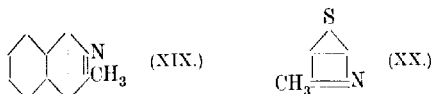
The condensations of the quaternary salts may thus be supposed to be effected through these methylene bases, which contain the reactive grouping  $\text{-Nalk-}\ddot{\text{C}}\text{:CH}_2$ , as indicated in the following scheme:



whilst 3-methylisoquinoline and 2-phenyl-4-methylthiazole are non-reactive because they are incapable of corresponding tautomeric changes, for these would involve the formation of compounds of such formulæ as :



From this, the conclusion would be drawn that in compounds with condensed nuclei like quinoline and *isoquinoline* only such changes take place in the heterocyclic ring as are compatible with the retention by the benzenoid ring of its full aromatic character; and also, probably, that bridged modifications such as XIX and XX (the precursors of the forms XVI and XVIII) are not produced to



any appreciable extent in the intramolecular vibrations of the *isoquinoline* or the thiazole nucleus.

The behaviour of the chloro-derivatives of *isoquinoline* is of interest in this connexion. It seems to be a general rule that when in a methyl compound, R·CH<sub>3</sub>, the radicle R is of such a nature that the methyl group shows enhanced reactivity, then in the corresponding chloro-compound, RCl, the chlorine also will be unusually reactive.\* It would therefore be expected that the chlorine atoms in 1-chloro*isoquinoline* and 3-chloro*isoquinoline* would show a difference of reactivity parallel to that shown by the methyl groups in the two corresponding methyl*isoquinolines*. Experiments of Gabriel and Colman have shown that such a difference does indeed exist.

Whilst 1-chloro*isoquinoline* gives a good yield of *isoquinoline* when heated for three hours with hydriodic acid and red phosphorus at 170–180° (Gabriel and Colman, *Ber.*, 1900, **33**, 986), 3-chloro*isoquinoline* is not reduced under these conditions; for when 1:3-dichloro*isoquinoline* is heated with the same reagents at 170° the 1-chlorine atom only is removed and the resulting 3-chloro*isoquinoline* resists further reduction. Complete removal of the chlorine so as to produce *isoquinoline* could only be effected by heating with red phosphorus at 200° (Gabriel, *Ber.*, 1886, **19**, 1655).

\* Compare, for example, acetone and acetyl chloride; 2:4-dinitrotoluene and 2:4-dinitrochlorobenzene; quinaldine and 1-chloroquinoline.

It might be suggested that such reductions are effected through the formation and decomposition of additive products and that the difference in the mobility of the chlorine in the two positions would be accounted for if, as is probable, 1:2 (or 1:4)-additive products of isoquinoline are comparatively readily produced whilst 2:3-additive products cannot be formed. The unequal mobility of the chlorine atoms seems to us, however, rather to indicate a difference in chemical polarity of the carbon atoms to which they are attached, probably dependent on a difference between the linkings on the two sides of the nitrogen atom such as is indicated in the formula with the alternate single and double bonds.

## EXPERIMENTAL.

### A. Derivatives of 1-Methylisoquinoline.

**1-Methylisoquinoline.**—This base was prepared by the dehydration of  $\omega$ -acetylaminophenylmethylcarbinol by means of phosphoric oxide in boiling xylene according to the method devised by Pictet and Gams (*Ber.*, 1910, **43**, 2384), the carbinol, in quantities of 3 grams, being dissolved in 50–60 c.c. of hot xylene and boiled gently for twenty minutes with 20–25 grams of phosphoric oxide. The preparation of aminomethylphenylcarbinol ( $\beta$ -hydroxy- $\beta$ -phenylethylamine) by reduction of benzaldehydecyanohydrin and its acetylation were carried out as described by Wolfheim (*Ber.*, 1914, **47**, 1440).

**1-Styrylisoquinoline**,  $C_9H_8N \cdot CH:CHPh$ .—A mixture of 1-methylisoquinoline with an equimolecular proportion of benzaldehyde and a small amount of the zinc chloride compound of the base was heated in a sealed tube at  $100^\circ$  for twenty hours. Water separated, and the contents of the tube crystallised in long needles on cooling. On recrystallisation from alcohol the styrylisoquinoline was obtained in almost colourless needles, which melted at  $111^\circ$  (Found: C = 88.26; H = 5.78.  $C_{17}H_{13}N$  requires C = 88.31; H = 5.63 per cent.).

**1-Methylisoquinoline Methiodide.**—This quaternary salt, which has not been previously described, was prepared by heating the base with methyl iodide in a sealed tube at  $60^\circ$  for six hours. It is also formed almost quantitatively when a mixture of the base and methyl iodide is allowed to remain at the ordinary temperature for twenty-four hours. On recrystallisation from absolute alcohol, in which it is readily soluble, the methiodide was obtained in almost colourless needles, melting at  $207.5^\circ$  (Found: I = 44.44.  $C_{11}H_{12}NI$  requires I = 44.56 per cent.). The compound is sparingly soluble in cold, easily soluble in hot water.

1-*p*-Dimethylaminostyrylisoquinoline Methiodide,  
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH} \cdot \text{C}_8\text{H}_6\text{N}(\text{CH}_3)\text{I}$ .

—A solution of 1-methylisoquinoline methiodide (2.2 grams), *p*-dimethylaminobenzaldehyde (1.1 grams), and piperidine (0.3 c.c.) in absolute alcohol (30 c.c.) gave a red colour immediately on heating, and after boiling for three hours red crystals (0.8 gram) separated. These were filtered from the hot solution, and after boiling for four hours more, a further 1.2 grams of crystals were obtained. On recrystallisation from methyl alcohol, the dyestuff was obtained in light red needles with a faint blue reflex. It melted and decomposed at  $257^\circ$ , although the melting point varied with the rate of heating (Found: C = 57.75; H = 5.03; N = 6.78; I = 30.62.  $\text{C}_{20}\text{H}_{21}\text{N}_2\text{I}$  requires C = 57.69; H = 5.05; N = 6.73; I = 30.53 per cent.). The colour in dilute solution is orange; it is discharged by acidification with mixed acids, but reappears on dilution or addition of alkali.

The dyestuff is a weak photosensitiser; the extra sensitiveness conferred on the gelatino-bromide plate extends approximately to the D line for moderate exposures. Its photo-sensitising action is considerably weaker than that of the isomeric 2-*p*-dimethylaminostyrylquinoline methiodide.

When 1-methylisoquinoline methiodide is heated with nitroso-dimethylaniline and piperidine in alcoholic solution, a deep ruby colour is developed. It is therefore to be concluded that condensation takes place with the formation of an azomethine derivative. When the methiodide is heated with alcoholic soda and quinoline methiodide, an intense red colour develops in a few minutes, and the solution shows the double absorption band in the green, characteristic of the *isocyanines*, whence it appears likely that 1-methylisoquinoline methiodide, like quinaldine methiodide, can undergo the *isocyanine* condensation. Owing to lack of material, these reactions were not further investigated.

### B. 3-Methylisoquinoline.

3-Methylisoquinoline.—This base was prepared from *o*-cyanophenylacetoneitrile according to the method described by Gabriel and Neumann (*Ber.*, 1892, 25, 3563). By acetylation, treatment with sodium hydroxide and then with sulphuric acid, *o*-cyanophenylacetoneitrile is converted into 3-methylisocarbostyryl, and from this 3-methylisoquinoline may be obtained, either by converting it into the 1-chloroisoquinoline and reducing this with hydriodic acid in sealed tubes, or by distillation with zinc dust in a stream of hydrogen. We found the reduction by zinc dust to be the better method, as it gives practically as good a yield and is much quicker.



*3-Methylisoquinoline and Benzaldehyde.*—This base could not be made to condense with benzaldehyde in the presence of anhydrous zinc chloride.

3-Methylisoquinoline (0.7 gram), benzaldehyde (1.01 grams), and a granule of anhydrous zinc chloride were heated in a sealed tube for forty-four hours at 100°; there was no indication of the formation of water, and the contents of the tube could not be induced to solidify on cooling.

The liquid in the tube was dissolved in ether and extracted several times with dilute sulphuric acid. The separated ethereal solution was found to contain 0.90 gram of benzaldehyde, and on the addition of alkali to the sulphuric acid solution, the unchanged base (0.5 gram) melting at 66° was obtained. This was converted into the picrate, which melted at 197°. (The pure base melts at 66°, and the picrate at 197°.)

*3-Methylisoquinoline Methiodide.*—This compound, which has not been previously described, was obtained by heating the base with methyl iodide in a sealed tube at 50° for four hours. On recrystallisation from absolute alcohol, in which it is easily soluble, the methiodide was obtained in lustrous, golden needles, which melted at 219° (Found: I = 44.49.  $C_{11}H_{12}NI$  requires I = 44.56 per cent.). It is easily soluble in hot water or hot dilute alcohol.

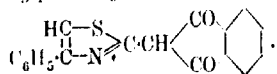
This methiodide could not be made to condense either with *p*-dimethylaminobenzaldehyde or with nitrosodimethylaniline in alcoholic solution in the presence of piperidine, nor would it condense with quinoline methiodide in presence of alcoholic sodium hydroxide solution to give a cyanine dye.

#### C. Derivatives of 4-Phenyl-2-methylthiazole.

*4-Phenyl-2-styrylthiazole.*—4-Phenyl-2-methylthiazole was prepared from acetamide and phenacyl bromide as described by Hantzsch (*Annalen*, 1889, **250**, 269).

On heating an equimolecular mixture of this base and benzaldehyde with a granule of anhydrous zinc chloride in a sealed tube for thirty-six hours at 100°, water separated, and the contents of the tube crystallised in long needles on cooling. On recrystallisation from absolute alcohol, the substance was obtained in colourless, shining needles, melting at 131.5° (Found: C = 77.20, 77.44; H = 4.94, 5.20.  $C_{17}H_{13}NS$  requires C = 77.56; H = 4.95 per cent.).

*4-Phenyl-2-thiazolylphthalonylmethane,*



—4-Phenyl-2-methylthiazole (4 grams), phthalic anhydride (3 grams), and anhydrous zinc chloride (3 grams) were heated in a sealed tube for six hours at  $190^{\circ}$ . The contents of the tube dissolved readily in concentrated sulphuric acid at  $100^{\circ}$ , and on pouring this solution into much water, a brown powder was precipitated, which was collected and washed. It was recrystallised from glacial acetic acid, in which it is readily soluble, when the phthalone was obtained in dark brown needles. On recrystallisation of this from absolute alcohol, in which it is sparingly soluble, the dyestuff was obtained in light brown, shining needles, which melted at  $257^{\circ}$  (Found:  $N = 4.5$ .  $C_{18}H_{11}O_2NS$  requires  $N = 4.6$  per cent.).

The substance is quite insoluble in caustic soda, and its dilute solution in alcohol dyes silk a faint yellow shade. It is almost insoluble in ether, and it is considerably deeper in colour than the corresponding quinophthalone.

*4-Phenyl-2-methylthiazole Methiodide*,  $C_{10}H_9NS, CH_3I$ .—This methiodide was made by heating the base with methyl iodide in a sealed tube at  $80^{\circ}$  for twenty-four hours. On recrystallisation from hot water, in which it is easily soluble, the methiodide was obtained in colourless, shining needles, melting at  $202^{\circ}$ . It is easily soluble in hot absolute or dilute alcohol (Found:  $I = 40.07$ .  $C_{11}H_{12}NIS$  requires  $I = 40.07$  per cent.).

*4-Phenyl-2-p-dimethylaminostyrylthiazole Methiodide*.—On heating a solution of 4-phenyl-2-methylthiazole methiodide (7 grams) and *p*-dimethylaminobenzaldehyde (3.3 grams) in absolute alcohol (80 c.c.) with piperidine (1 c.c.), a red colour developed immediately, and after boiling for forty minutes, red crystals (5 grams) were deposited from the boiling solution, and a further 1 gram separated at the end of the hour. On recrystallisation from methyl alcohol, the dyestuff was obtained in ruby-red crystals with a bluish-green metallic reflex. It melts and decomposes at  $243^{\circ}$ , but the melting point varies with the rate of heating (Found:  $C = 53.43$ ;  $H = 4.90$ ;  $I = 28.39$ ;  $S = 7.18$ .  $C_{20}H_{21}N_2IS$  requires  $C = 53.57$ ;  $H = 4.69$ ;  $I = 28.35$ ;  $S = 7.14$  per cent.).

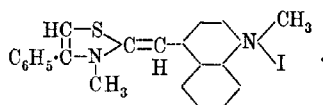
The colour in dilute solution is a deep orange, and is discharged by acids, but reappears on dilution or addition of alkali. The dyestuff is a photosensitiser, and the extra sensitiveness conferred on the gelatino-bromide plate extends to  $\lambda 6200$ , with a maximum at  $\lambda 5500$  for moderate exposures.

*4-Phenylthiazole-2-aldehyde p-Dimethylaminoanil Methiodide*.—A solution of 4-phenyl-2-methylthiazole methiodide (5 grams) and nitrosodimethylaniline (2.5 grams) in absolute alcohol (90 c.c.) gave a red colour in the cold on the addition of piperidine (0.15 c.c.), and after boiling for fifteen minutes, bright green crystals (6 grams)

separated from the boiling solution, and about half a gram more was obtained after a further four hours' boiling. On recrystallisation from methyl alcohol, the dyestuff was obtained in red crystals with an intense green metallic reflex. It melted and decomposed at  $228^{\circ}$ , but the melting point varied somewhat with the rate of heating (Found: C = 50.60; H = 4.58; I = 28.45; S = 7.07.  $C_{19}H_{20}N_3IS$  requires C = 50.77; H = 4.46; I = 28.29; S = 7.13 per cent.).

The colour in solution is a deep ruby-red, which is discharged by acids with great ease, but reappears on dilution or addition of alkali.

4-Phenyl-3-methyl-2-thiazolanyl-4-quinolylmethane Methiodide,



—A solution of 4-phenyl-2-methylthiazole methiodide (4 grams), quinoline methiodide (7.2 grams), and sodium hydroxide (0.71 gram) in absolute alcohol (80 c.c.) gave an intense red colour on heating, and after boiling for thirty minutes, a semi-crystalline precipitate was formed on cooling. On recrystallisation from methyl alcohol, the cyanine dyestuff was obtained in red crystals with a bluish-green metallic reflex, melting and decomposing at  $240^{\circ}$  (Found: I = 27.73; S = 6.73.  $C_{21}H_{19}N_2IS$  requires I = 27.83; S = 6.99 per cent.).

The colour in solution is a deep orange-red, and is discharged by acidification, but reappears on dilution or addition of alkali. The dyestuff is a photosensitiser, and the extra sensitiveness conferred on the gelatino-bromide plate extends to  $\lambda$  6000, with a maximum at  $\lambda$  5300, for moderate exposures.

D. 2-Phenyl-4-methylthiazole.

2-Phenyl-4-methylthiazole and Benzaldehyde.—2-Phenyl-4-methylthiazole was made from thiobenzamide and monochloroacetone, according to the method described by Hubacher (*Annalen*, 1890, 259, 236), and was found to boil at  $282^{\circ}/762$  mm. Hubacher describes it as a liquid: we obtained it in colourless crystals melting at  $29.5^{\circ}$ .

This base failed to react with the equivalent amount of benzaldehyde in the presence of anhydrous zinc chloride, when heated in a sealed tube for ninety-six hours at  $100^{\circ}$ . The unchanged base melting at  $29^{\circ}$  was recovered from the acid aqueous extract of the contents of the tube, and the ethereal extract, on oxidation with potassium permanganate, yielded an amount of benzoic acid

corresponding with 90 per cent. of the benzaldehyde originally taken.

*2-Phenyl-4-methylthiazole Methiodide*.—This quaternary salt was obtained in a 70 per cent. yield by heating the base with methyl iodide in a sealed tube for forty-eight hours at 90°.

It is formed with far less readiness than the methiodide of the isomeric 4-phenyl-2-methylthiazole, an almost theoretical yield of which was obtained when the base was heated with methyl iodide for twenty-four hours at 80°. The difference of reactivity towards alkyl iodides of the nitrogen in the two systems,  $\text{:CMe:N:CPh-}$  and  $\text{:CPh:N:CMe-}$ , in which the methyl and phenyl groups are interchanged, is noteworthy.

On recrystallisation from hot water, in which it is fairly soluble, the methiodide was obtained as faintly yellow prisms which melted at 192°. It is easily soluble in hot dilute or absolute alcohol (Found:  $\text{I} = 40.16$ .  $\text{C}_{11}\text{H}_{12}\text{NIS}$  requires  $\text{I} = 40.07$  per cent.).

When this methiodide (4 grams) and *p*-dimethylaminobenzaldehyde (2 grams) were boiled in absolute alcoholic solution (40 c.c.) with piperidine (0.4 c.c.) for fifteen hours, the solution assumed the brownish-red tinge which is produced when an alcoholic solution of *p*-dimethylaminobenzaldehyde is boiled for a long time with piperidine, but no evidence that any condensation had taken place could be obtained.

On evaporation of the alcohol, a red, semi-crystalline, tarry mass remained, which was well washed with ether and extracted several times with boiling water. In the aqueous solution was found the unchanged methiodide (3.8 grams). In a similar manner, it was proved that, after six hours' boiling of the methiodide and nitrosodimethylaniline with piperidine in alcoholic solution, no condensation had taken place; thus showing a great contrast with the methiodide of 4-phenyl-2-methylthiazole, which gave an 85 per cent. yield of condensation product with nitrosodimethylaniline in the presence of piperidine after boiling the alcoholic solution for only fifteen minutes. No condensation of 2-phenyl-4-methylthiazole methiodide with quinoline methiodide in alcoholic soda solution could be effected.

One of us (J. L. B. S.) is indebted to the Department of Scientific and Industrial Research for a grant which he desires gratefully to acknowledge. He also wishes to express his thanks for a grant from the Government Grant Committee of the Royal Society by which part of the cost of the materials employed was defrayed.

UNIVERSITY CHEMICAL LABORATORY,  
CAMBRIDGE.

[Received, November 15th, 1922.]

CCCXXIX.—*Preparation of  $\alpha$ -Trioxymethylene and a New Polymeride of Formaldehyde.*

By DALZIEL LLEWELLYN HAMMICK and ALFORD REGINALD BOEREE.

PRATESI (*Gazzetta*, 1885, **14**, 139) prepared  $\alpha$ -trioxymethylene,  $(\text{CH}_2\text{O})_3$ , a colourless, crystalline substance melting at  $61^\circ$ . He obtained it by heating the amorphous, polymerised form of formaldehyde known as paraform with "a trace" of sulphuric acid in a sealed tube at  $115^\circ$ .

Pratesi's work could not be repeated by Kraut (*Annalen*, 1890, **258**, 95), by Auerbach and Barschall (*Arb. Kais. Gesundheit. Amt*, 1905—6, **27**, 220), or by Dunlop (*T.*, 1914, **105**, 1155). Auerbach and Barschall (*loc. cit.*), however, prepared the substance by subliming paraform (or a mixture of  $\beta$ - and  $\gamma$ -polyoxymethylenes) in a slow current of nitrogen into a small quantity of ice-water. They give  $63$ — $64^\circ$  as the melting point of the pure substance, purified by recrystallisation from ether or by sublimation.

Attempts to repeat Pratesi's method of preparation using "dry" paraform (containing about 1 per cent. of moisture) met with no success. Moreover, many experiments were carried out before the precise conditions were found under which the substance could be prepared in reasonable yields by Auerbach and Barschall's method. As described below, it has, however, been found possible to prepare  $\alpha$ -trioxymethylene in about 10 per cent. yield by a modification of Pratesi's method, in which considerable quantities of sulphuric acid and water are used instead of "a trace" of acid. Directions are also given for preparing the substance in a yield of about 20 per cent. by Auerbach and Barschall's method.

*$\alpha$ -Polyoxymethylene: a New Polymeride of Formaldehyde.*

$\alpha$ -Trioxymethylene, purified by repeated sublimation at  $46^\circ$  in a bent, closed and exhausted tube, was found to melt at  $64^\circ$ . After eight sublimations, a trace of moisture apparently still remained (as indicated by mistiness forming on the cool parts of the tube before the deposition of the slender needles of  $\alpha$ -trioxymethylene occurred). The last traces of water were removed by recrystallisation from sodium-dried ether, which was evaporated by a current of dry air. The crystals thus obtained melted at  $64^\circ$ , as before; but on resubliming at  $46^\circ$  in an exhausted tube the dry substance was found to behave differently from the slightly moist preparation. The sublimate appeared in the form of large, stout prisms instead of the usual long needles. Many of the prisms were not entirely

transparent but contained white, opaque regions. On inverting the tubes and resubliming,  $\alpha$ -trioxymethylene passed to the cold end of the tube, leaving behind a white, silky, paper-like substance. By repeated sublimation, the whole of the  $\alpha$ -trioxymethylene was converted into this substance (Found: C = 39.9; H = 6.6.  $[\text{CH}_2\text{O}]_n$  requires C = 40.0; H = 6.7 per cent.).

The compound is thus a polymeride of formaldehyde ( $\epsilon$ -polyoxymethylene). It is doubly refracting, although it possesses no distinct crystalline form. It melts with decomposition and depolymerisation at 195–200° (uncorr.). On heating in an open tube, the smell of formaldehyde is noticed and a white sublimate is obtained which melts at 163°. This substance is probably one (or several) of the polyoxymethylenes described by Auerbach and Barschall (*loc. cit.*), all of which melt below 170°.

$\epsilon$ -Polyoxymethylene is insoluble in water, sodium sulphite solution, and the usual organic solvents. Like the other polyoxymethylenes, it dissolves in boiling nitrobenzene and separates as an amorphous powder on cooling. No measurable depression of the freezing point of nitrobenzene was found. On boiling with ammoniacal silver nitrate, the surface of the substance blackens, but no silver mirror is obtained and the liquid remains clear; in this respect, the new polymeride is clearly differentiated from the previously known polymerides. It could not be acetylated by the method of Barnett (*J. Soc. Chem. Ind.*, 1921, 40, 8r) and therefore probably contains no hydroxyl groups.

*Preparation of  $\alpha$ -Trioxymethylene: Modification of Pratesi's Method.*

Paraformaldehyde (10 parts) and a mixture of equal volumes of sulphuric acid and water (1 part) were placed at the bottom of glass tubes (18"  $\times$  1") closed at one end. The open ends were drawn out and sealed after exhaustion of the tubes by the water-pump. The ends of the tubes containing the formaldehyde-acid mixture were immersed in an oil-bath at 115°. Long, slender needles began almost immediately to form in the cool parts of the tubes. After about fifteen minutes, the tubes were removed, the portions containing the crystalline  $\alpha$ -trioxymethylene cut off, and the crystals scraped out.

Owing to the fact that methyl formate and other volatile liquids are produced in the tubes (Dunlop, *loc. cit.*) the heating in the oil-bath must be stopped as soon as liquids begin to condense on the cool parts of the tubes. If this precaution is not taken, the  $\alpha$ -trioxymethylene is washed out of the upper portions of the tubes and cannot be regained.

The yields obtained by this method, after purification by resub-

limination, were about 10 per cent. calculated on the formaldehyde used.

*Preparation of  $\alpha$ -Trioxymethylene: Auerbach and Barschall's Method.*

The success of Auerbach and Barschall's method was found to depend on the volume of the "small quantity of water" into which the above workers sublimed paraformaldehyde. They do not specify the actual amount of water used; it was found, however, that 40 grams of ice-water per 100 grams of paraformaldehyde (or  $\beta$ - and  $\gamma$ -polyoxymethylenes) gave the most satisfactory results.

As found by Auerbach and Barschall, the mixture of  $\beta$ - and  $\gamma$ -polyoxymethylenes obtained by slowly adding 4 volumes of concentrated sulphuric acid to 10 volumes of 40 per cent. "formalin" and keeping for two days in the ice-chest, gave better yields of  $\alpha$ -trioxymethylene than crude paraform. The mixture of polyoxymethylenes was placed in a round flask fitted with a cork carrying a tube for leading in a current of carbon dioxide and a short, wide, bent tube leading below the surface of ice-water in a test-tube immersed in ice and water. The flask was heated rapidly to 200° in an oil-bath, a slow current of carbon dioxide being maintained through the apparatus until the contents of the flask had passed into the ice-water.

The ice-water solution was distilled with the aid of a short fractionating column. If too little water had been used to absorb the products of the sublimation of the polyoxymethylenes in carbon dioxide, the condensate was jelly-like and on distillation choked the column and condenser with solid products. Too much water led to poor yields. With the quantities given above (100 of  $\beta$ - and  $\gamma$ -polyoxymethylene to 40 of water in the receiver) the product distilled easily and gave a substance which on the addition of sodium chloride and extraction with ether yielded  $\alpha$ -trioxymethylene to the extent of about 20 per cent. calculated on the original polymerised formaldehyde.

*Summary.*

- i.  $\alpha$ -Trioxymethylene can be prepared by heating paraformaldehyde in sealed tubes with water and sulphuric acid.
- ii. The conditions necessary for the successful use of Auerbach and Barschall's method for the preparation of  $\alpha$ -trioxymethylene are recorded.
- iii. A new polymeride of formaldehyde,  $\epsilon$ -polyoxymethylene, is obtained by the repeated sublimation of dry  $\alpha$ -trioxymethylene.

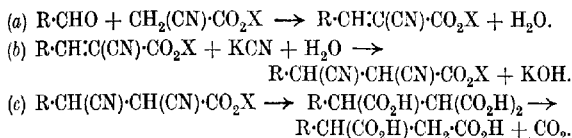
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OXFORD.

[Received, November 4th, 1923.]

CCCCXX.—*Syntheses of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. Part II. Preparation of Acids containing Saturated Aliphatic Residues and the Constitution of the Aliphatic Alkylidenecyanoacetic Esters.*

By ARTHUR LAPWORTH and JOHN ALEXANDER McRAE.

IN Part I (this vol., p. 1699), the authors dealt with some synthetic processes for preparing substituted  $\alpha$ -cyanoacrylic acids from sodium chloroacetate, potassium or sodium cyanide, and aldehydes containing aromatic residues, and mainly in connexion with the conversion of  $\alpha$ -cyanoacrylic acids into the substituted succinic acids through their hydrogen cyanide additive products. Omitting the first stage in the synthetic process used, namely, the production of potassium or sodium cyanoacetate from the chloroacetate and cyanide, the stages involved may be summarised by means of the following schemes :



Equations (a), (b), and (c) are of general applicability and X may be H or alkyl. The paper mentioned dealt only with cases where X = H.

The present communication deals with aspects of these processes which present themselves when aldehydes and ketones containing the group,  $\cdot\dot{\text{C}}\text{H}\cdot\dot{\text{C}}\text{H}\cdot\text{CO}\cdot$ , characteristic of the majority of the more familiar aliphatic carbonyl compounds, are used.

At the outset of these experiments it was clear that in aldehydes and ketones of this type, new complications might arise owing to several circumstances which are absent when aldehydes such as benzaldehyde, piperonal, etc., are used. In order that these circumstances may be made clear, it is necessary to refer in some detail to the theory of the synthetic processes which seem to be involved.

The ethylenic linkage is normally associated with a high reactivity towards the halogens, ozone, or permanganate, reagents which may be said to belong to Class I, and the compounds in which it occurs are as a rule profoundly and permanently affected by these reagents. On the other hand, it shows no appreciable reactivity towards



potassium cyanide, sodium hydrogen sulphite, or hydroxylamine, reagents which may be said to belong to Class II. The carbonyl group, on the other hand, is not permanently altered by reagents of Class I, but forms additive compounds of fairly permanent character with reagents of Class II.

When, however, an ethylenic linkage occurs in the  $\alpha$ -position with respect to the  $\cdot\text{CO}\cdot$  or  $\cdot\text{CN}$  group, it exhibits properties which may be described as intermediate between those of the normal ethylenic linkage and those of the carbonyl group, for it then not only assumes the power of uniting with agents of Class II, towards which in other situations with regard to these groups it is apparently inert, but what is equally significant, its activity towards agents of Class I falls off to a marked degree.

The capacity of the ethylenic linkage in unsaturated aldehydes, ketones, and nitriles to unite with the agents of Class II\* is well known to organic chemists, and the low activity towards agents of Class I, although probably less familiar, could scarcely escape the notice of those who have frequent occasion to handle such  $\alpha\beta$ -unsaturated compounds. Bauer (*Ber.*, 1904, **37**, 3317) directed attention to the inhibiting effect on the addition of bromine, of  $\cdot\text{CO}_2\text{H}$ ,  $\cdot\text{CO}_2\text{Alk}$ , and  $\cdot\text{CN}$  in certain unsaturated compounds; Sudborough and Thomas (*T.*, 1910, **97**, 715) made measurements of the speed of absorption of bromine by various types of unsaturated carboxylic acids and found that the  $\beta\gamma$ - and  $\gamma\delta$ -unsaturated acids reacted many thousands of times more rapidly than the  $\alpha\beta$ -unsaturated isomerides.

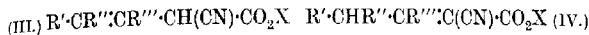
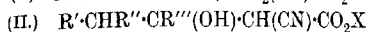
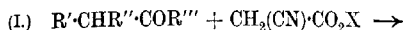
The authors are not aware of any instance in which a single ethylenic linkage is capable of taking up the elements of the reagents of Class II, except when situated in the  $\alpha\beta$ -position with respect to  $\cdot\text{CO}\cdot$  or  $\cdot\text{CN}$ , though doubtless  $\cdot\text{NO}_2$  and  $\cdot\text{SO}_2\text{Alk}$  would be effective in the same way as these groups.

It is on such considerations that the views hereinafter expressed are based. In the first instance, they point to the conclusion that only  $\alpha\beta$ -unsaturated cyanoacetic acids and esters (IV in the following scheme) are directly concerned in the synthesis of succinic acids by Br  dt and Kallen's and Lapworth's methods, and that the  $\beta\gamma$ -unsaturated acids and esters (III in the following scheme) are not capable of uniting with potassium, sodium, or hydrogen cyanide or other reagents of Class II except after transformation into the  $\alpha\beta$ -unsaturated isomerides.

The scheme which follows represents reactions which may be

\* To the agents of Class II may be added compounds such as nitromethane, ethyl malonate, and ethyl acetoacetate (compare the Michael and allied reactions) and their sodio-derivatives.

assumed to occur when an aliphatic aldehyde or ketone (I) is condensed with cyanoacetic acid or its ester.

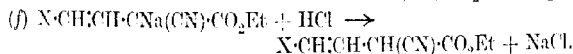
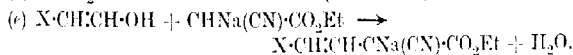
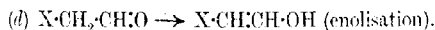


where  $X = H, C_2H_5$ , etc., and  $R', R'',$  and  $R''' = H, CH_3$ , etc.

It will no doubt be very generally accepted that the "aldol," II, is probably the first of the series of definite intermediate products and that III or IV, if formed at all, are products of subsequent, possibly reversible, changes and are perhaps mutually intraconvertible.

At the outset of the research, it seemed probable that (II) might prove much more stable than the corresponding products,  $Ar \cdot CH(OH) \cdot CH(CN) \cdot CO_2X$ , formed from aromatic aldehydes (compare Part I). It was found, however, that in each case tried the products of addition of hydrogen cyanide to (IV) were, in fact, formed, and therefore it became clear that there was no real arrest at stage (II). There remained the question whether (II) is to a greater or less extent transformed into (III) and whether (III) accumulates or is transformed into (IV) in the conditions used.

There were some *a priori* reasons for thinking that formation of (III) might account for the low yields of succinic acid derivatives formed when aliphatic aldehydes and ketones were used. Previous authors have concluded that the unsaturated esters which are made by condensing aliphatic aldehydes and ketones of type (I) with ethyl sodio-cyanoacetate and decomposing the resulting sodio-derivatives with water or acids are  $\beta\gamma$ -unsaturated esters, and held that they were formed by reactions such as the following:



Here equation (e) originated in a hypothesis first put forward by Rogerson and Thorpe (T., 1905, **87**, 1685) and its apparent applicability here was considered to support that hypothesis.

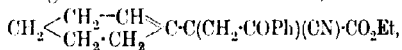
The conclusion that the esters in question are  $\beta\gamma$ -unsaturated derivatives (Harding, Haworth, and Perkin, T., 1908, **93**, 1943; Haworth, *ibid.*, 1909, **95**, 480; Gardner and Haworth, *ibid.*, 1909,

95, 1955; Harding and Haworth, *ibid.*, 1910, 97, 486) was based on the fact that when the esters are hydrolysed and the product converted into monocarboxylic acids with loss of carbon dioxide the monocarboxylic acids are of the  $\beta\gamma$ -unsaturated type. Braun (*Monatsh.*, 1896, 17, 218) and Strassmann (*ibid.*, 1897, 18, 722) have previously obtained analogous results on elimination of carbon dioxide from alkylidenecyanoacetic acids (compare also Knoevenagel and his pupils, *J. pr. Chem.*, 1918, [ii], 97, 288).

The present authors decided that they were likely to obtain most definite light on the processes taking place in their syntheses by studying the properties of the supposed  $\beta\gamma$ -unsaturated alkylidenecyanoacetic esters, but were surprised to find that the behavior of these towards agents of Class I and Class II corresponded closely with that of the  $\alpha\beta$ -unsaturated type, to which there can now be little or no doubt they must, in fact, be referred. Apart from the fact that the esters made by the condensation of the aldehyde and ketones with ethyl sodiocyanoacetate do not appear to differ in any way from the esters formed on condensing these with ethyl cyanoacetate itself by the employment of various agents such as piperidine in small quantities, the following points may be cited in favour of the view that the unsaturated esters in question are of the  $\alpha\beta$ - and not of the  $\beta\gamma$ -type:

(1) These esters do not unite rapidly with bromine or ozone and this peculiarity is, as has already been indicated, characteristic of  $\alpha\beta$ -unsaturated forms.

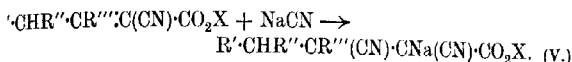
(2) Like the other esters in question, that made by condensing cyclohexanone with cyanoacetic ester is very inert towards bromine or ozone. By the action of phenacyl bromide on its sodio-derivative however, it yields a crystalline phenacyl derivative which reacts very readily with these agents, but not with cyanides or bisulphites. This phenacyl derivative, therefore, has properties which show that it does not belong to the same type as the parent ester, and this view is in agreement with the constitution,



which was assigned to it by Harding, Haworth, and Perkin (*T.*, 1908, 93, 1958). The distinction in properties between this and the parent ester is readily understood only if, as is now maintained, the latter has the structure  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 & \text{CH}_2 \\ & \diagdown & \diagup \\ & \text{CH}_2 & \text{CH}_2 \end{smallmatrix} > \text{C} \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$ .

(3) The esters are attacked very readily by solutions of potassium or sodium cyanide, yielding metallo-derivatives (V), stable in aqueous solution, identical with those obtained in another way by Higson and Thorpe (*T.*, 1906, 89, 1455) and, like the compounds

first isolated by these workers, convertible by hydrolysis, with loss of carboxyl, into substituted succinic acids. As has been pointed out above, ready combination at an ethylenic linkage with potassium, sodium, or hydrogen cyanide is characteristic of  $\alpha\beta$ -unsaturated carbonyl compounds or nitriles. The metallo-derivatives in question are no doubt formed in accordance with the following equation, which the conventional formula, with sodium attached to carbon, also used by Higson and Thorpe, is for convenience adopted:



(4) They yield additive products with sodium hydrogen sulphite readily, dissolving rapidly in not too concentrated solutions of this salt in the cold. This reaction, like other processes of addition of strongly polar agents to ethylenic linkages, is characteristic of  $\alpha\beta$ -unsaturated esters, acids, ketones, aldehydes, etc.

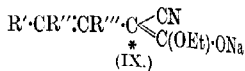
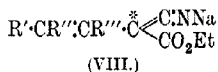
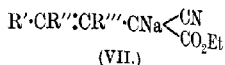
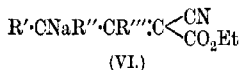
(5) When ethyl heptylidenecyanoacetate is oxidised with ozone in the presence of water, it yields heptaldehyde without any detectable quantity of hexaldehyde. Had the  $\beta\gamma$ -unsaturated ester,  $\text{H}_{11}\text{CH}:\text{CH}:\text{CH}(\text{CN})\cdot\text{COEt}$ , been present in appreciable amount, it would have been oxidised much more readily than the  $\alpha\beta$ -unsaturated ester (compare I above), and hexaldehyde would readily have been detected. The ester made by condensing acetone with ethyl cyanoacetate, like ethyl heptylidenecyanoacetate and all the other esters of the series which have been examined from this point of view, reacts slowly with ozone, and the products which are obtained by decomposing the ozonide with water are only such as would be obtained from the  $\alpha\beta$ -unsaturated ester,  $(\text{CH}_3)_2\text{C}:\text{C}(\text{CN})\cdot\text{COEt}$ , which would afford (Scheiber and Meisel, *Ber.*, 1915, 48, 238).

The following is the explanation which the present authors consider to be the only one consistent with all the data so far as they are known:

The condensation products of ethyl cyanoacetate with aliphatic aldehydes and ketones which contain the group  $-\dot{\text{C}}\text{H}\cdot\text{CO}-$  have a very labile molecular system. The free esters have the structure  $\text{CHR}''\text{CR}'''\text{C(CN)CO}_2\text{Et}$ , whatever the structure of the sodio-derivatives may be, although the presence of small quantities of  $\beta\gamma$ -isomerides in equilibrium with the  $\alpha\beta$ -isomerides which constitute the large bulk of the fluid esters is not necessarily excluded.

The structure of the sodio-derivatives is more problematical, especially as no final decision has yet been reached by chemists on the question of the constitution of such compounds as ethyl

sodiocyanoacetate itself. At least four structures suggest themselves in the present instance, namely :



and possibly a mixture of all four of these is present in solutions of the sodio-derivatives. If, however, the possibility of such sodio-derivatives existing with sodium attached directly to carbon be not admitted, then either (VIII) or (IX), or both, must be adopted, and this requires that the sodio-compound is derived from the  $\beta\gamma$ -isomeride of the free ester (V). The present authors, whilst not inclined wholly to adopt the latter view, consider that the bulk at least of the dissolved metallo-compound is derived from the  $\beta\gamma$ -form of the ester. The properties of the alkylated cyano-esters obtained by the action of alkyl iodides and bromides on the sodio-derivatives correspond with those of  $\beta\gamma$ -unsaturated esters (that is, VII, with Na replaced by Alk).

In (V), the formula deduced for the free esters, the ethylenic linkage appears conjugated with unsaturated centres in the cyano- and carbethoxy-groups. In (VIII) and (IX), the most probable formulæ for the sodio-derivatives, the ethylenic linkage again appears conjugated, but with the double linkages denoted by the signs \*\*. The lability of structure in these products is no doubt associated with the tendency to retain conjugated structures and with the powerful induced polarities due to the simultaneous and homogenous influence of the powerful cyano- and carbethoxy-groups (compare X and XI).

Whilst the high reactivity of the free esters towards hydrogen sulphite and cyanide might have been attributed to the occurrence of a preliminary isomeric change from a  $\beta\gamma$ - to an  $\alpha\beta$ -unsaturated type, their low reactivity towards ozone and bromine decides against that interpretation of the data.

The authors have not succeeded in isolating the pure alkylidene-cyanoacetic acids from the very mixed products which are obtained when aliphatic aldehydes and ketones are condensed with sodium cyanoacetate in aqueous solution. So far as all the indications derived from the results of the experiments can be interpreted, it would appear that the free acids and their salts, like the esters,

\* It may be observed here that (VIII) corresponds with Nef's formula for ethyl sodio-cyanoacetate and (IX) with Thorpe's.



are entirely consistent with the views expressed in the present paper. In all cases, those cyanoglutaconic esters which contain the grouping  $\cdot\dot{C}C(CN)\cdot CO_2Et$ , or are capable of conversion into isomerides which contain this complex by mere migration of the double bond and transference of a hydrogen atom, react with potassium cyanide solution. Ethyl  $\alpha$ -cyano- $\alpha\beta$ -trimethylglutaconic ester,  $CO_2Et\cdot CMe(CN)\cdot CMe\cdot CMe\cdot CO_2Et$ , a  $\beta\gamma$ -unsaturated cyanoacetic ester which cannot undergo the required preliminary change, is inert. It is evident that even potassium cyanide solution may cause migration of the double bond in unsaturated cyanoacetic esters, and in dealing with this class of compounds it is now abundantly clear that conclusions based on the apparent "directness of the facts" (compare Farmer, this vol., p. 2016) must be subjected to very strict scrutiny.

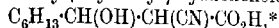
#### EXPERIMENTAL.

##### (A) *Condensation of Aliphatic Aldehydes and Ketones with Sodium Cyanoacetate.*

(1) *Heptaldehyde.*—When purified heptaldehyde is shaken with somewhat less than one molecular proportion of sodium cyanoacetate in water which has been made slightly alkaline with sodium hydroxide, the mixture after a few minutes assumes an appearance which suggests that a salt has begun to crystallise out, but soon afterwards the whole becomes homogeneous. In the latter case, very little heating takes place, but if a considerable excess of sodium hydroxide is used, a marked rise in temperature takes place. Similar results are also observed if piperidine in small or large quantity respectively is used as condensing agent. The origin of the secondary heat effect has not been discovered, but it may possibly be due to acceleration of the stage represented by equation II (p. 2743), that is, the elimination of water from the intermediate hydroxylic or aldol-like condensation product.

The mixed acids obtained by condensing heptaldehyde with sodium cyanoacetate in aqueous solution under a variety of conditions have been isolated and subjected to a prolonged examination in the hope of ascertaining their true character. It is unnecessary to enter into detail, and sufficient to state that the product appears to be of a very mixed character, is highly viscous, and shows very little tendency to deposit crystals; it slowly loses water on exposure in a desiccator, and if titrated after about a month against standard alkali, has an "equivalent" which is

approximately 184. It is perhaps a mixture of heptylidene-*cyanoacetic acid* and possibly  $\beta$ -hydroxy- $\gamma$ -cyanononoic acid,



with other more complex products. Fiquet's heptylidene-*cyanoacetic acid* (m. p. 114°) was not isolated, but on one occasion a small quantity of a sodium salt separated during the condensation of the heptaldehyde and sodium cyanoacetate which gave an impure crystalline acid (m. p. 85–92°) having the chemical characteristics of Fiquet's acid. Aniline hydrochloride, which was found to be excellent as condensing agent in the case of benzaldehyde and sodium cyanoacetate (this vol., p. 1701), was useless in the present instance.

A considerable number of experiments were made on the reduction of the crude products with sodium amalgam, as the aromatic cyanoacrylic acids may readily be converted into their dihydro-derivatives in this way. Thus it was hoped that the heptylidene-*cyanoacetic acid*, for example, might be converted into heptyl-*cyanoacetic acid* and this into nonoic acid or its nitrile by suitable treatment. There was apparently little action and no more than traces of these products were found. Subsequent experiments in these laboratories have shown that the reduction of the aliphatic cyanoacrylic acids by means of sodium amalgam follows quite a different course from that expected, and the subject will be dealt with in later communications.

(2) *Acetaldehyde*.—The acid products obtained by condensing acetaldehyde with sodium cyanoacetate in aqueous solution resemble those from heptaldehyde, and no pure constituent was isolated. The equivalent of the viscous acid product after evaporating the ethereal solution obtained on extracting it from the acidified reaction mixture was about 141, whilst  $\text{CH}_3\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CO}_2\text{H}$  requires 111. Thus the crude acid appears to contain an impurity of high molecular weight. The crude product was, in this case, further investigated by shaking it with sodium hydrogen sulphite, which readily converts the  $\alpha\beta$ -unsaturated esters into stable additive products (compare p. 2745). From 13.7 grams of crude acids there were isolated 2.7 grams (20 per cent.) of a material insoluble in the aqueous solution; on acidifying the aqueous solution and extracting with ether, 6.3 grams (45 per cent.) of a viscous acid were obtained which after exposure for some time in a desiccator over sulphuric acid had an equivalent of roughly 135 [the hydroxy-

\* Experiments made by one of us (J. A. M.) on the mixture obtained by condensing ethyl cyanoacetate with heptaldehyde, using magnesium methyl iodide to detect the presence of hydroxyl, did not furnish any evidence of the presence of appreciable quantities of the hypothetical aldol-like compound.



acid,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$ , requires 129]. Thus only some 54 per cent. of the product behaved as the  $\alpha\beta$ -unsaturated acid was expected to do, namely, to remain dissolved in the acidified sodium hydrogen sulphite solution and to be incapable of being extracted from it by ether. It will be shown later that at least 42–53 per cent. of the acetaldehyde used in such a condensation may be converted into methylsuccinic acid.

(B) *Conversion of the Crude Alkylidenecyanoacetic Acids into Alkylsuccinic Acids.*

(1) *n*-*Hexylsuccinic Acid from Heptaldehyde*.—Oenanthal (25 grams) is condensed with sodium cyanoacetate as made from 25 grams of monochloroacetic acid by the process described by Phelps and Tillotson (*Amer. J. Sci.*, 1908, [iv], **26**, 267), using 4 c.c. of 20 per cent. caustic soda as condensing agent. After half an hour or longer, the liquid is shaken with a little ether to remove unchanged oenanthal, made neutral by addition of acetic acid, and finally mixed with potassium cyanide (18.9 grams) in water (60 c.c.) and acetic acid (14.6 grams) in water (30 c.c.), the total volume being 350 c.c. The whole is allowed to remain five days at room temperature, when it is made thoroughly acid with hydrochloric acid, the oily deposit extracted with ether, and after evaporation of the latter, hydrolysed by means of fuming hydrochloric acid (150 c.c., saturated at  $0^\circ$ ), first in the cold and finally at the boiling point. The semi-solid acid formed is easily collected and washed with water. It becomes crystalline after prolonged boiling with dilute nitric acid, which removes most of the impurities, and was identified as hexylsuccinic acid (m. p.  $82^\circ$ ). Higson and Thorpe, T., 1906, **89**, 1470, gave m. p.  $87^\circ$ ; the yield of crude product was 60 per cent. of that theoretically possible from the quantity of heptaldehyde used.

The somewhat impure *n*-hexylsuccinic acid was converted through the anhydride into the anilic acid; this, when recrystallised from benzene, melted at  $121^\circ$  (Higson and Thorpe, *loc. cit.*, gave m. p.  $121^\circ$ ). The equivalent found was 280;  $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , requires 277.

*n*-*Hexylsuccinimide*,  $\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CO} \begin{smallmatrix} \diagup \\ \text{CH}_2 \end{smallmatrix} \text{CO} \diagdown \text{NH}$ .—This was prepared by converting the acid into its ammonium salt (well-formed crystals with a fatty texture), and distilling this under a pressure of 12 mm., when it passed over at  $160\text{--}190^\circ$  and solidified in the receiver. The imide separated from benzene on addition of light petroleum in clusters of silky needles melting at  $91^\circ$  (Found: N = 7.8.  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$  requires N = 7.65 per cent.).

(2) *Methylsuccinic Acid from Acetaldehyde*.—On replacing heptaldehyde in the preceding condensation by acetaldehyde, it was found that the titre of unchanged cyanide in the second part of the process fell only very slowly\* and the process was therefore accelerated by heating the solution for ten hours on the water-bath. The product was acidified with excess of hydrochloric acid, evaporated to dryness, the residue being then hydrolysed with fuming hydrochloric acid, finally on the water-bath, until evolution of carbon dioxide ceased. The methylsuccinic acid was isolated by evaporating to dryness and extracting in a Soxhlet apparatus with acetone; it became semi-solid after boiling with dilute nitric acid and cooling, and in this crude condition represented a yield of about 53 per cent. of the theoretical quantity calculated on the weight of acetaldehyde used. In a second experiment under similar conditions, a yield of 42 per cent. of practically pure methylsuccinic acid (m. p. 110°) was isolated.

(C) *Attempted Extension to Ketones.*

Preliminary experiments made in the hope of extending the application of the use of solutions of crude sodium cyanoacetate for the preparation of dialkylsuccinic acids from ketones were made and evidence was obtained that dimethylsuccinic acid could be obtained from acetone in this way, but in very small yield only. No appreciable quantity of a substituted succinic acid was obtained from cyclohexanone. The contrast between these results and those with aldehyde are in accordance with the fact that  $\beta\beta$ -disubstituted acrylic acids are formed less readily than the  $\beta$ -monosubstituted acids and also react much less readily with additive reagents (compare this vol., p. 51).

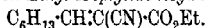
*Investigation of some Aliphatic Alkylidenecyanoacetic Esters.*

In view of the great practical difficulties encountered in studying the very mixed products obtained by condensing aliphatic aldehydes with salts of cyanoacetic acid it was thought desirable, before proceeding further along these lines, to concentrate on one of the several problems involved, and as the esters of the alkylidenecyanoacetic acids are the only derivatives of the intermediate products which have previously been isolated in a pure condition, the study of these was taken up. Owing to the difficulty experienced in separating pure ethyl ethylidenecyanoacetate from

\* It has recently been shown by Higginbotham and Lapworth (this vol., p. 49) that free unsaturated acids take up hydrogen cyanide much more slowly than the corresponding esters.

unchanged ethyl cyanoacetate the experiments did not include the former compound.

(1) *Experiments on Ethyl Heptylidencyanoacetate,*



—This substance was made by condensing ethyl cyanoacetate and heptaldehyde in molecular proportions with the aid of piperidine (about 1 drop per 4.5 grams of mixture) at room temperature for three hours and working up the product by dissolving it in ether, washing out the piperidine with dilute acid and water successively, drying, and fractionating three times under reduced pressure. The ester boiled at 144–145°/13 mm. and represented a yield of 32 per cent. of the theoretical quantity; of the remainder, about an equal weight could be distilled over at 190°/13 mm.

Ethyl heptylidencyanoacetate (ethyl  $\alpha$ -cyano- $\beta$ -*n*-hexylacrylate) reacts very slowly with bromine at the ordinary temperature. When boiled with alcoholic potassium hydroxide, it gives off ammonia and heptaldehyde.

When the ester is shaken with a moderately dilute solution of sodium hydrogen sulphite for a few minutes, it dissolves completely except for a trace of oily impurity; if the solution used is very concentrated, the additive product is salted out as an oil which instantly dissolves on addition of water.\* It has not been found possible to regenerate the ester from the resulting solution nor has the additive product in this instance been isolated in a crystalline condition.

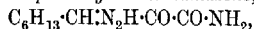
If a solution of potassium cyanide be substituted for one of sodium hydrogen sulphite, somewhat similar results are obtained: the product is the stable and soluble potassium derivative of the dicyano-ester,  $\text{C}_6\text{H}_{13}\cdot\text{CH}(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$  (compare Higson and Thorpe, T., 1906, 89, 1455), which is precipitated as an oil on addition of mineral acid. On hydrolysing this crude oil by means of hydrochloric acid, hexylsuccinic acid may be obtained in quantity corresponding with 85 per cent. of the possible amount calculated on the ethyl heptylidencyanoacetate originally taken.

Addition of sodium ethoxide to an alcoholic solution of the ester at once gives rise to a golden-yellow coloration, doubtless due to the formation of the sodio-derivatives of the isomeric  $\beta$ -ester (compare p. 2746).

The ester reacts very slowly with ozone. In one experiment, a stream of ozonised oxygen was passed through 5 grams of the ester for sixteen hours, the product was then warmed gently with water to decompose any ozonide formed, and the whole subjected

\* Later experiments have shown that some of these additive products may be obtained readily enough in crystalline form.

to distillation in a current of steam. The first 50 c.c., which smelled strongly of heptaldehyde, was diluted to 300 c.c. with water and mixed at 90° with a solution of 1 gram of semioxamazide in 300 c.c. of water. The precipitate obtained was collected, washed with water, and recrystallised from 85 per cent. alcohol; it weighed 0.9 gram, softened at 224° and melted at 227°, and had all the properties of *heptaldehydesemioxamazone*,



in admixture with a sample of which the melting point was unchanged (Found: N = 21.1.  $\text{C}_9\text{H}_{17}\text{O}_2\text{N}_3$  requires N = 21.2 per cent.).

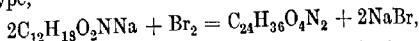
It may be added that the later part of the distillate from the decomposition of the ozonide contained only a trace of heptaldehyde together with unchanged ester. The absence of any appreciable quantity of hexaldehyde in the distillate and therefore of  $\beta\gamma$ -unsaturated ester in the original heptylidenecyanoacetic ester thus appears certain.

When the yellow solution made by mixing heptylidenecyanoacetic ester in alcoholic solution with sodium ethoxide (1 mol.) was heated with benzyl chloride for several hours, the ester was converted into an oily mixture from which no large fraction of constant boiling point could be obtained. It was clear that the reaction is a complex one, and analysis of one fraction, boiling at 176–178°/12 mm., indicated that it was a mixture of ethyl  $\alpha$ -cyano- $\alpha$ -benzyl- $\Delta^8$ -nonenoate,  $\text{C}_5\text{H}_{11}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CH}_2\text{Ph})(\text{CN})\cdot\text{CO}_2\text{Et}$ , and the nitrile,  $\text{C}_5\text{H}_{11}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CN}$ , probably arising from the former under the influence of sodium ethoxide with loss of ethyl carbonate (compare Ingold and Thorpe, T., 1919, 115, 143). It was inert toward solutions of potassium cyanide or sodium hydrogen sulphite.

An attempt to prepare a crystalline phenacyl derivative by substituting  $\omega$ -bromoacetophenone for benzyl chloride in the operation described in the preceding paragraph (compare Harding, Haworth, and Perkin, T., 1908, 93, 1958 and this vol., p. 2755) was not in this case successful.

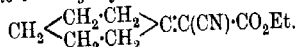
On adding bromine (1 mol.) to the solution made by mixing ethyl heptylidenecyanoacrylate and sodium ethoxide in equimolecular proportions, a precipitate of sodium bromide was at once produced, but some bromine remained free. The ester was found to be converted into a viscid liquid which could not be distilled undecomposed and which on analysis by Robertson's method was found to contain only 16 per cent. of bromine in place of the 27.7 per cent. which is required for the monobromo-derivative of the original ester. As the product instantly liberated iodine from

acidified potassium iodide, it is probable although not certain that the bromine was present in the  $\alpha$ -position and not the  $\gamma$ -position. The non-utilisation of a full molecular proportion of bromine in the above experiment and the low content of bromine in the product are probably to be accounted for by the occurrence of a reaction of the type,



corresponding with the well-known conversion of ethyl sodioacetate into ethyl diacetylsuccinate.

(2) *Experiments on Ethyl cycloHexyldienecyanoacetate,*

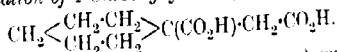


—This substance was selected as one more likely to be persistent in the  $\beta\gamma$ -unsaturated form,  $CH_2 < \begin{matrix} CH_2 - CH \\ CH_2 \cdot CH_2 \end{matrix} > C \cdot CH(CN) \cdot CO_2Et$ , which structure was the one selected for it by Harding, Haworth, and Perkin (T., 1908, 93, 1956), who accordingly termed it ethyl  $\alpha$ -cyano- $\Delta^1$ -cyclohexeneacetate.

The ester was made by one of the methods described by the previous workers (*loc. cit.*, p. 1958), the yield being 53 per cent. It boiled at 160—163°/15 mm. This ester dissolves quickly when shaken with a strong aqueous solution of potassium cyanide. Dilute sodium hydrogen sulphite solution dissolves it completely in the course of twelve hours. Bromine and also ozone react with it very slowly.

Two grams of the ester were subjected to the action of a current of strongly ozonised oxygen for four days, the ozonide formed being subsequently decomposed by hot water and the product subjected to distillation with a current of steam. The greater part of the ester seemed to be unchanged, but the first portion of the distillate smelled strongly of cyclohexanone and yielded the *p*-nitrophenylhydrazone (m. p. 144°) of that compound without difficulty. The latter substance was identified further by analysis (Found: N = 18.2 per cent.). The ketone is not found in the steam distillate in appreciable quantity when the ester has been ozonised for a few hours only.

*Action of Potassium Cyanide on Ethyl cycloHexyldienecyanoacetate. Formation of 1-Carboxycyclohexyl-1-acetic Acid,*

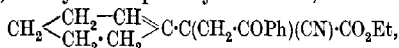


—Ethyl cyclohexyldienecyanoacetate (10 grams) was dissolved in 50 c.c. of 95 per cent. alcohol, and to this was added potassium cyanide (7.0 grams = 2 mols.) in 15 c.c. of water; a considerable rise in temperature took place. The mixture was allowed to stand

two days, after which the alcohol was distilled off. On acidifying, an oil was precipitated which soon became crystalline. This precipitate was treated with fuming hydrochloric acid (80 c.c.), saturated at 0°, and after remaining over-night in the ice-chest the whole was heated under reflux until evolution of carbon dioxide ceased. On cooling, an oil, which quickly became crystalline, separated; this weighed 7.6 grams, corresponding with 88 per cent. of the calculated quantity. The crude acid was recrystallised several times from hot water with the aid of animal charcoal, when it melted constantly at 132°. It crystallised in plates. A portion heated with resorcinol and zinc chloride gave, on addition of alkali, a solution showing intense green fluorescence (Found: C = 57.84; H = 7.50; equivalent by titration, 93.  $C_9H_{14}O_4$  requires C = 58.07; H = 7.53 per cent., equivalent = 93).

*Reactions of a True  $\beta\gamma$ -Unsaturated Cyanoacetic Ester.*

In order to obtain direct evidence bearing on the assumption that a  $\beta\gamma$ -unsaturated cyanoacetic ester of the type represented by Harding, Haworth, and Perkin for ethyl cyclohexylidenecyanoacetate would behave towards ozone much like an ordinary ethylenic compound, the crystalline phenacyl derivative,



described by them, was prepared. This is certainly a  $\beta\gamma$ -unsaturated ester and, as was anticipated, was found to react with ozone very readily; when a slow current of ozonised oxygen was passed through a solution of 2 grams of this compound in 5 c.c. of dry chloroform, a marked rise of temperature took place and in a few minutes the solution was entirely changed in properties, presenting the appearance of a thick jelly. It may be added that this compound also took up bromine with avidity in marked contrast with the behaviour of the parent  $\alpha\beta$ -unsaturated ester, and was inert towards solutions of potassium cyanide or sodium hydrogen sulphite.

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formation in each case of the isomeric ortho- as well as the well-known para-hydroxyazo-compound. This simultaneous formation of the *o*-isomeride has been observed previously in only two cases (compare Bamberger, *Ber.*, 1900, **33**, 3188).

The corresponding hydroxybisazo-compounds have been prepared, but the hydroxytrisazo-compounds which are formed by the further interaction of the diazonium salt and the hydroxybisazo-compounds have not been isolated as they are difficult to free from the bis-compounds, which they closely resemble in properties; the unsubstituted 2:4:6-trisbenzeneazophenol, which is more easily purified, has been isolated by Grandmougin and Freimann (*Ber.*, 1907, **40**, 2662).

The ortho-hydroxyazo-compounds are formed in very small amounts relatively to the para. They may easily be isolated by taking advantage of their slight volatility in steam, the para-isomerides not being volatile in steam.

The hydroxybisazo-compounds are formed by adding a cooled solution of the diazonium salt to a cooled alkaline solution of either the *o*- or *p*-hydroxyazo-compound and subsequently acidifying. The hydroxytrisazo-compounds are produced similarly from an alcoholic alkaline solution of the 2:4-bisbenzeneazo-compounds.

#### EXPERIMENTAL.

*4'-Chloro-2-benzeneazophenol*,  $C_6H_4Cl \cdot N_2 \cdot C_6H_4 \cdot OH$ .—Ten grams of *p*-chloroaniline, dissolved in 20 c.c. of concentrated hydrochloric acid and 60 c.c. of water, were diazotised and slowly added with constant stirring to 8 grams of phenol dissolved in enough 20 per cent. caustic soda to ensure the mixed liquids remaining alkaline. After some five minutes' standing, acetic acid was added in slight excess and the mixture of 4'-chloro-2- and -4-benzeneazophenol, which was thrown down as a light pink, finely divided precipitate, was filtered off and exhaustively steam distilled for about five hours. The ortho-compound, which only came over slowly in small amount, separated from the distillate in the condenser and receiver as a light yellow solid.

The yield of ortho-compound amounted to about 1 per cent.\* of the theoretical, the other 99 per cent. consisting of the long-known para-compound.

To purify the crude product it was again steam distilled and finally recrystallised from alcohol, in which it is easily soluble and from which it separates in long, very slender prisms of a bright reddish-orange colour, *m. p.* 117·5°.

It is moderately easily soluble in most organic solvents and in alkali giving a yellow solution, but it is insoluble in water and



dilute acids (Found: Cl = 15.38.  $C_{12}H_9ON_2Cl$  requires Cl = 15.24 per cent.). The deep red para-compound remaining after steam distillation was used as the starting material for the preparation of the bis-compound.

The other 2-azophenols described were prepared by the same method with slight necessary modifications.

*4'-Bromo-2-benzeneazophenol*,  $C_6H_4Br \cdot N_2 \cdot C_6H_4 \cdot OH$ , was prepared from *p*-bromoaniline and phenol and isolated exactly as described above. The yield obtained was about 0.6 per cent. of the theoretical. It is readily soluble in alcohol, and crystallises in slender prisms of a bright reddish-orange colour decidedly redder in shade than those of the corresponding chloro-compound; m. p. 133.5° (Found: Br = 29.10.  $C_{12}H_9ON_2Br$  requires Br = 28.84 per cent.).

*4'-Iodo-2-benzeneazophenol*,  $C_6H_4I \cdot N_2 \cdot C_6H_4 \cdot OH$ , crystallises from alcohol, in which it is somewhat sparingly soluble, in long, very slender, needle-like prisms of a bright scarlet colour, m. p. 139°. The yield was about 0.6 per cent. of the theoretical (Found: I = 39.30.  $C_{12}H_9ON_2I$  requires I = 39.17 per cent.). The increase of the red shade in the colour of these compounds with the rise in atomic weight of the halogen is worth noting.

*2-o-Tolueneazophenol*,  $C_6H_4Me \cdot N_2 \cdot C_6H_4 \cdot OH$ .—Coupling in this case, the only one in which an ortho-substituent was present in the aniline, was much slower than in the others. On mixing, no colour appeared till several minutes had elapsed, and the reaction was not so clean as in the other cases, some tarry matter separating on acidification. The yield of the ortho-compound was only about 0.4 per cent. of the theoretical, the well-known para-compound being again the chief product.

*2-o-Tolueneazophenol* is readily soluble in boiling alcohol and separates in long, very slender, needle-shaped crystals of a beautiful golden-red colour, m. p. 88° (Found: N = 13.24.  $C_{13}H_{12}ON_2$  requires N = 13.21 per cent.).

The hydroxybisazo-compounds are all easily made by adding a solution of a diazonium salt to an alkaline solution of either an hydroxy-*o*- or an hydroxy-*p*-azo-compound and subsequently acidifying. They are all solids of a dull brown colour which are not very readily dissolved by boiling organic solvents and which separate on cooling as microcrystalline powders. They all dissolve in aqueous alkalis, forming deep brownish-red solutions.

*4' : 4''-Dichloro-2 : 4-bisbenzeneazophenol*,  $OH \cdot C_6H_3(N_2 \cdot C_6H_4Cl)_2$ .—This compound is produced when a solution of *p*-chlorobenzene-diazonium chloride is added to an alkaline solution either of 4'-chloro-2- or -4-benzeneazophenol. It is moderately easily soluble in boiling glacial acetic acid, giving a brown solution,

from which it separates on cooling in nodular aggregates of minute crystals. It melts with decomposition at 210-211° (Found: Cl = 19.09.  $C_{18}H_{12}ON_4Cl_2$  requires Cl = 19.06 per cent.). Its constitution was established by reducing it in glacial acetic acid solution with tin and hydrochloric acid. After removing the tin by hydrogen sulphide, a colourless solution was obtained which somewhat rapidly oxidised and became reddish-brown. On evaporation to dryness, a reddish-brown, crystalline mass was left which, when heated for some minutes with acetic anhydride, yielded the triacetyl-2:4-diaminophenol, m. p. 180°, described by Kehrman and Bahatryan (*Ber.*, 1898, **31**, 2399).

As this bis-compound can be obtained either from the previously described compound melting at 117.5° or from the well-known 4'-chloro-4-benzeneazophenol, the former must have the ortho-configuration assigned to it.

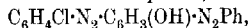
The constitution of the other ortho-azo and bisazo-compounds described was similarly established.

4':4''-Dibromo-2:4-bisbenzeneazophenol,  $OH \cdot C_6H_3(N_2 \cdot C_6H_4Br)_2$ , separates from boiling glacial acetic acid, in which it is sparingly soluble, in yellowish-brown, crystalline nodules similar to those of the bischloro-compound but somewhat darker in shade. It resembles the corresponding chloro-compound closely in properties and melts with decomposition at 224° (Found: Br = 35.40.  $C_{18}H_{12}ON_4Br_2$  requires Br = 34.74 per cent.).

4':4''-Di-iodo-2:4-bisbenzeneazophenol,  $OH \cdot C_6H_3(N_2 \cdot C_6H_4I)_2$ , separates from boiling glacial acetic acid, in which it is very sparingly soluble, in nodular crystalline aggregates of a dark brown colour, m. p. 208° (Found: I = 45.94.  $C_{18}H_{12}ON_4I_2$  requires I = 45.81 per cent.).

A number of isomeric bis-derivatives containing different azo-groups have been prepared.

4-p-Chlorobenzeneazo-2-benzeneazophenol,



forms minute crystals of a yellow-brown colour, m. p. 165° (Found: Cl = 10.61.  $C_{18}H_{13}ON_4Cl$  requires Cl = 10.53 per cent.).

2-p-Chlorobenzeneazo-4-benzeneazophenol crystallises in small, yellow crystals, m. p. 133° (Found: Cl = 11.70.  $C_{18}H_{13}ON_4Cl$  requires Cl = 10.53 per cent.).

4-p-Bromobenzeneazo-2-benzeneazophenol forms aggregates of minute, brown crystals, m. p. 178° (Found: Br = 21.30.  $C_{18}H_{13}ON_4Br$  requires Br = 20.97 per cent.).

2-p-Bromobenzeneazo-4-benzeneazophenol forms nodular aggregates of small, brown crystals, m. p. 147° (Found: Br = 21.00.  $C_{18}H_{13}ON_4Br$  requires Br = 20.97 per cent.).

4-p-Iodobenzeneazo-2-benzeneazophenol forms aggregates of minute, dark brown crystals, which decompose on heating at about 160° (Found: I = 29.70.  $C_{18}H_{13}ON_4I$  requires I = 29.64 per cent.).

2-p-Iodobenzeneazo-4-benzeneazophenol crystallises in nodules of minute, dark brown crystals, m. p. 119° (Found: I = 30.02.  $C_{18}H_{13}ON_4I$  requires I = 29.64 per cent.).

2-p-Bromobenzeneazo-4-p-tolueneazophenol forms aggregates of minute, light brown crystals, m. p. 192° (Found: Br = 20.64.  $C_{19}H_{15}ON_4Br$  requires Br = 20.22 per cent.).

4-p-Bromobenzeneazo-2-p-tolueneazophenol forms aggregates of minute, light brown crystals, m. p. 213° (Found: Br = 20.30.  $C_{19}H_{15}ON_4Br$  requires Br = 20.22 per cent.).

It may be noted as an interesting point in connexion with these mixed bisazo-compounds that in every case the compound with the azo-group containing the halogen in the para-position has a much higher melting point than its isomeride.

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## CCCXXXII.—*The Behaviour of the Stannic Acids towards Solutions of Alkaline Hydroxides.*

By GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD.

In a former paper (this vol., p. 444) dealing with the structure of the stannic acids, the authors put forward the hypothesis that  $\beta$ -stannic acid is a salt-like complex formed by a continued process of condensation between molecules of stannic hydroxide acting as acid and base, respectively. In a second paper (this vol., p. 1122), it was pointed out that the hypothesis would lead one to expect that the more complex varieties of stannic acid would be capable of being resolved into less condensed forms by the action of strong acids and bases, an expectation which is in accordance with well-established facts. In the paper referred to, the behaviour of the stannic acids towards hydrochloric acid was fully discussed; the present communication deals with the results of experiments in which different modifications of stannic acid have been submitted to the action of solutions of alkaline hydroxides.

The general principles which underlie the action of alkalis upon the stannic acids are similar to those which have been fully discussed in connexion with the action of hydrochloric acid upon the same substances (*loc. cit.*). Although it is impossible, owing

to the rapidity with which subsequent changes take place, to obtain an adsorption isotherm, it is probable that alkali is first of all adsorbed by the stannic acid and that this adsorption is followed by chemical action between the two substances. This chemical action, as in the case of the behaviour towards hydrochloric acid, may follow two courses, the one leading, under favourable conditions, to the peptisation of the stannic acid, and the other bringing about the gradual disintegration of the original complex acid and leading to the formation of a less condensed modification of stannic acid.

The chief difference between the action of alkaline hydroxides and that of hydrochloric acid on the stannic acids lies in the fact that both peptisation and the reversal of the  $\alpha$ - $\beta$  change are brought about more easily by the former reagents than by the latter; such behaviour is quite in accordance with what has been previously stated with reference to the relative values of the basic and acidic affinities of stannic hydroxide (this vol., p. 444). Owing to the acidic properties being the more highly developed, a given sample of stannic acid will tend to form salts with adsorbed alkalis which are more stable and less liable to suffer hydrolysis than those formed with adsorbed acids. As peptisation takes place as a result of the electrical charge which the complex acquires through the ionisation of these salts, it is evident that a solution of potassium hydroxide will be a more efficient peptising agent than a solution of hydrochloric acid of equivalent concentration, for the simple reason that the former substance will be able to form a larger amount of salt than the latter, and so lead to the complex becoming more highly charged than is possible with the acid reagent.

On the other hand, owing to the acidic properties of stannic hydroxide being more highly developed than the basic ones, it naturally follows that the salt-like complex resulting from the condensation of stannic hydroxide will be more readily decomposed by a solution of potassium hydroxide than by one of hydrochloric acid of similar concentration.

Since peptisation of the stannic acids by acids and alkalis is brought about in accordance with the same general principles, it follows that the comparative behaviour of different modifications of stannic acid towards alkaline hydroxides will be analogous to that shown towards hydrochloric acid. The critical concentration of alkali necessary to bring about the peptisation of a sample of stannic acid will therefore be the greater the more condensed the acid is, that is, the more completely it has acquired the  $\beta$ -nature. Conversely, the  $\beta$ -sols should be more readily coagulated by the addition of an excess of alkali than the sols formed from the  $\alpha$ -acid,

as the repression of the ionisation of the alkaline salt of the  $\beta$ -acid and consequent reduction of the charge carried by the complex particles, would be more readily brought about than with the salt of the  $\alpha$ -acid. Various observations in the literature are in agreement with the conclusion drawn above regarding the relative ease of peptisation of different modifications of stannic acid. Thus, whilst Heinz (Dissertation, Göttingen, 1914) found that sols of  $\alpha$ -stannic acid could be obtained in which the ratio of  $K_2O$  to  $SnO_2$  was 1 : 200, Franz (Dissertation, Göttingen, 1913) found that the ratio in  $\beta$ -sols was 1 : 25 or 1 : 50. Again, although both  $\alpha$ - and  $\beta$ -stannic acids have been described as soluble in a solution of potassium hydroxide, a differentiation in their solubility was made by Kühl (*Pharm. Ztg.*, 1908, **53**, 49), who showed that a preparation of stannic acid in which the  $\alpha$ - $\beta$  change had progressed to a considerable extent required a solution of potassium hydroxide of greater concentration to dissolve it than was necessary with a less condensed sample of the acid.

Whilst there appears little doubt that the principles which govern the action of alkaline hydroxides upon stannic acid are independent of the particular alkali employed, it must be noted that the changes observed with sodium hydroxide differ very considerably from those which accompany the action of potassium hydroxide. This difference in behaviour, which is fully described in the experimental part of the paper, is probably due to the difference in the solubility of the sodium and potassium salts of stannic acid, Zocher (*Z. anorg. Chem.*, 1920, **112**, 1) having shown sodium stannate to be less soluble than the potassium salt. In view of the lower solubility of the sodium salt, a smaller concentration of sodium hydroxide than of potassium hydroxide would be able to bring about the coagulation of sols produced as a result of the peptisation of stannic acid by the two hydroxides respectively.

#### EXPERIMENTAL.

The samples of the different modifications of stannic acid which were employed were prepared by the methods which have been described in the previous paper dealing with the hydrochloric acid experiments (*loc. cit.*).

Two series of experiments were conducted; in the one, weighed amounts of the different preparations of the acid were treated with a concentrated solution of potassium hydroxide (14.3N) and afterwards diluted, whilst in the other quantities of  $\beta$ -stannic acid were treated with dilute solutions of potassium hydroxide of various degrees of concentration. The mixtures were maintained at a temperature of 25°.

In both series of experiments it was found that with the higher concentrations of alkali (0·8—1·1N) a portion of the  $\beta$ -stannic acid was undispersed, whereas with the  $\alpha$ -acid the whole of the substance added was dispersed in presence of potassium hydroxide of the above concentration. This difference in behaviour was attributed to the greater ease with which the  $\beta$ -sols undergo coagulation, the ionisation of the salt formed by adsorption of the alkali by the acid being repressed by the excess of potassium hydroxide remaining in solution. That this explanation is the correct one was shown by removing the apparently insoluble matter from the flasks containing the  $\beta$ -mixtures in question and adding it to distilled water, when it was found that the substance readily dispersed owing to there no longer being an excess of potassium ions present in the liquid. The critical concentration of potassium hydroxide above which coagulation of  $\beta$ -sols takes place is 0·78N; this is a much lower concentration than was observed with hydrochloric acid as peptising agent, for in such cases no coagulation occurred with a solution having a concentration of 1·5N.

In all those cases in which the whole of the initial quantity of stannic acid was dispersed, more of the requisite preparation was added to the mixture, and this process was repeated if such subsequent additions were, in their turn, completely dispersed. As more and more of the acid was added, the colour of the mixture became more intense, and the viscosity considerably increased. With this increase in viscosity the rate of dispersion of the solid diminished and it became possible to observe the intermediate stages of the process. The fine powder added first caked together and gradually underwent transformation into a clear yellow gel which slowly dispersed into the supernatant liquid and gave, eventually, an apparently homogeneous system. The larger the amount of stannic acid which was added, the stiffer was the gel ultimately obtained; it was possible to obtain gels so stiff that they retained their shape when the containing flasks were inverted.

The composition of some of the gels obtained by the action of the more dilute solutions of potassium hydroxide on samples of tannic acid is shown in Table I; for the purpose of contrast, figures are also given showing the composition of the filtrate from systems in which the concentration of alkali used had been sufficiently great to repress the ionisation of the salt formed by adsorption of potassium hydroxide by the initial quantity of stannic acid. The alkalinity was determined by titration with a standard solution of hydrochloric acid, using methyl-orange as indicator, whilst the iron was estimated by titration with iodine after reduction to the stannous condition by means of aluminium and hydrochloric acid.

TABLE I.

Variety of acid.	Original normality of KOH.	Composition of gel per cent.	
		K <sub>2</sub> O.	SnO <sub>2</sub> .
$\alpha$	0.4	0.98	16.5
$\alpha$	0.8	1.99	28.4
$\beta$	0.49	1.42	25.8
$\beta$	0.6	1.68	27.2

Systems in which the initial amount of stannic acid was not wholly dispersed.

Variety of acid.	Original normality of KOH.	Composition of filtrate per cent.	
		K <sub>2</sub> O.	SnO <sub>2</sub> .
$\beta$	0.8	3.29	2.81
$\beta$	1.0	3.94	5.80

Attempts were made in several cases to determine the amount of tin in molecular solution by submitting the mixtures to ultra-filtration, but this was a much more difficult operation than with the hydrochloric acid systems owing to the action of the alkali on the collodion membranes. The best results were obtained by using films strengthened by means of calico; reinforced films of this kind were prepared by immersing a piece of the fabric in the solution of collodion and leaving it in position during the evaporation of the solvent. Some of the results obtained from mixtures containing  $\alpha$ -stannic acid are shown in Table II, the concentration of stannic oxide being expressed in gram-molecules per litre, whilst the alkalinity is expressed in normalities.

TABLE II.

Composition before ultra-filtration.		Composition of ultra-filtrate.	
OH'.	SnO <sub>2</sub> .	OH'.	SnO <sub>2</sub> .
0.009N	0.0116	0.005N	0.0023
0.150 "	0.888	0.061 "	0.284
0.304 "	1.53	0.115 "	0.542
0.458 "	1.90	0.172 "	0.527
0.661 "	2.48	0.399 "	1.53
0.732 "	3.04	0.348 "	1.10

Although the above results do not correspond with equilibrium conditions and so have no actual quantitative significance, it is possible to draw certain qualitative deductions from them. In every case the concentration of alkali is much reduced by the process of ultra-filtration, and this can only be accounted for by a large amount of the potassium hydroxide having been adsorbed by the colloidal stannic acid and removed along with the latter by the filtration through the collodion membrane. The total quantity of tin in the mixtures before ultra-filtration is much greater than in the viscous mixtures prepared by the agency of hydrochloric acid, this being accounted for by the much greater power of peptisation which potassium hydroxide has for stannic acid. Further, of the total tin present in the mixture, a larger proportion

passes into the ultra-filtrate than was the case with the hydrochloric acid mixtures, thus indicating that stannic acid can acquire a much higher degree of dispersion when acted upon by potassium hydroxide than is possible when a solution of hydrochloric acid of similar concentration is allowed to act upon the same variety of stannic acid.

*Action of Solutions of Sodium Hydroxide on Stannic Acid.*—Experiments similar to those which have been described above were made in which two varieties of stannic acid were acted upon by means of solutions of sodium hydroxide free from carbonate and chloride. None of the remarkable results which were obtained by the use of potassium hydroxide was observed to take place when sodium hydroxide was employed, a portion of the original amount of the stannic acid, whether  $\alpha$ - or  $\beta$ - in character, remaining undissolved in every case; no change in the appearance of the mixtures was observable during a period of seven months, the liquids remaining perfectly clear and mobile throughout the whole period. In Table III, the results of the analysis of the clear liquids, made 207 days from the commencement of the experiments, are given; as in previous cases, the concentration of stannic acid is expressed in gram-molecules per litre and the alkalinity was determined by titration with hydrochloric acid, with methyl-orange as indicator.

TABLE III.  
 $\alpha$ -Stannic acid.  $\beta$ -Stannic acid.

Initial normality of NaOH.	$\alpha$ -Stannic acid.		$\beta$ -Stannic acid.	
	OH' concn. in liquid.	SnO <sub>2</sub> .	OH' concn. in liquid.	SnO <sub>2</sub> .
0.209	0.179N	0.0065	0.208N	0.0033
0.418	0.417,,	0.0183	0.342,,	0.0105
0.627	0.592,,	0.0304	0.572,,	0.0250
0.836	0.789,,	0.0402		
1.045	0.988,,	0.0573	0.878,,	0.0899

The amount of tin in the most concentrated mixture containing  $\beta$ -stannic acid is abnormally high and may be due to the mixture not having arrived at equilibrium; it was unfortunately impossible to make a subsequent analysis.

It is evident from the above figures that a considerable amount of adsorption takes place, this being the explanation of the difference between the initial and the final alkalinity. Within the limits of concentration studied, the amount of tin dispersed increases with the concentration of the alkaline solution used. Moreover, the results obtained with the three most dilute solutions show that the  $\beta$ -acid is less soluble than the  $\alpha$ -variety, this being in agreement with what would be anticipated from theoretical considerations.



*The Significance of Crystal Structure.*A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON  
OCTOBER 26TH, 1922.

By SIR WILLIAM H. BRAGG, K.B.E., F.R.S.

It has long been perceived that every crystal is built up by the repetition throughout its volume of a certain unit. The repetition is exact in every detail, so that each unit is a perfect epitome of the whole. This idea is to be found in the writings of all the crystallographers: Barlow has expressed it very definitely:

"A homogeneous structure is one, every point within which, if we regard the structure as without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar . . ." (*Min. Mag.*, 1895, **11**, 119).

Barlow was certainly correct in his insistence on this as the fundamental point in crystal structure; and in putting into a secondary place the consideration of methods of dividing space into similar cells. Much attention has been directed to the latter question, but its interest belongs to geometry more immediately than to physics.

The conception of the unit cell—we may call it the *crystal unit*—being once adopted, the question of its contents arises immediately. Until the advent of the X-ray analysis there was no certain answer to the question; and in consequence further progress in the examination of the internal structure of crystals was practically blocked at the outset. It has sometimes been assumed that the unit is the chemical molecule, and much good experimental work has been described in terms of that conception. But such work can never bear its full fruit as long as it is rooted in an unsound idea. There is really no reason why the crystal unit should be identical with the chemical molecule; there is, in fact, every reason to expect the contrary.

The chemical molecule is the smallest portion of a substance which displays in full the properties of the substance. A pure substance consists of molecules which are all exactly alike; and there is nothing done by a crowd of them which each could not do to a lesser extent by itself. But the properties referred to in a definition of this sort are limited; the definition is incorrect if the limits are not carefully drawn. Broadly speaking, the properties are those which are possessed when the substance is in a liquid or a gaseous state and not in a solid state. A substance in the solid condition possesses a large number of properties which it does not possess as a liquid. Chemical analysis is based on the behaviour

of substances when their crystalline bonds have been broken up and the substance is found to be composed of units which are similar and behave similarly and are called molecules. It does not follow that each molecule, so identified, is capable by itself of representing the properties of the crystal. We know, in fact, of cases where it is not so. For example, the molecule of silicon dioxide is incapable, by itself, of producing the rotation of the plane of polarisation of light which is so characteristic of quartz. As a matter of fact, the crystal unit which does possess the property is made up of the substance of three molecules.

The crystal unit must contain the substance of an integral number of molecules; this is a simple consequence of the fact that the atoms of the different elements are present in the same proportion in both solid and liquid. We have no cause for assuming that the crystal unit contains the substance of one molecule only; nor have we cause for assuming that the molecule will be found in the crystal in exactly the same form and condition as in the liquid or gas.

The X-ray analysis shows that the unit nearly always contains the substance of more than one molecule, generally of two, three, or four. Further, it shows that the atoms in the unit can be divided into groups, each containing the substance of one molecule. The division may be very clear, as in the case of organic crystals; it may also be very faint or even indistinguishable, as in the case of rocksalt and diamond. The group may be spoken of as a molecule; but if so, it must be understood that the use of the term in the two cases does not imply that the relative dispositions of the atoms in the molecule of the crystal are the same as those of the atoms in the molecule of the liquid. We have good reason to believe that the "crystal molecule" differs very little from the ordinary molecule in many cases, but we may not assume them to be identical.

The definition of the crystal unit by the methods of X-ray analysis is quite precise. The form of the unit is necessarily a parallelepiped; it is bounded by three pairs of parallel faces. The distance between a pair, known as the "spacing" of the plane parallel to the pair, is determined by the law

$$\lambda = 2d \cdot \sin \theta,$$

where  $\lambda$  is the wave-length used,  $d$  is the spacing, and  $\theta$  is the smallest of the angles which the incident rays must make with the plane in order that reflexion may take place. Consequently, the measurement of a single angle determines the spacing in the case of each pair. This gives the volume of the unit. The

weight is found by multiplying by the density, and the number of molecules by dividing this weight by the weight of the molecule.

The shape of the unit has really an infinite number of alternatives. All the corners of the unit are exactly alike, in the sense that from each of them the outlook into the crystal is exactly the same. These corners, with all similar points throughout the crystal, make up the space lattice of the crystal. There is an infinite number of ways of choosing eight points on the latter which will be the corners of a parallelepiped containing no other similar point, and any one of these can be looked on as the crystal unit. They all contain the same number of molecules.

It is then to be asked whether the X-ray method is a trustworthy judge of the similarity of planes. Might there be some difference which is important to the structure of the crystal, but escapes detection by the X-rays?

Now it is true that the X-rays cannot distinguish between the two sides of a reflecting set of planes. Some time ago it was pointed out that in zinc blende, for example, it was impossible to differentiate the two ends of the polar crystal. If we move along a normal to the (111) planes of zinc blende, we come to layers of zinc and sulphur alternately: going one way, the distance from zinc to sulphur is three times the distance from sulphur to zinc; going the other way, the ratio reverses. The intensities of the various orders of reflexion of X-rays depend on the relative magnitudes of the spacings but not on their order, so that the (111) plane of zinc blende is the same both ways so far as X-rays are concerned. For the same reason, as has been pointed out more recently, the X-rays cannot differentiate directly a right-handed spiral from a left, since one is the reflexion of the other.

But these limitations do not affect the power to determine the size of the crystal unit without any uncertainty, so far as can be judged at present. There are, of course, difficulties of technique; some reflexion may be too small to be seen. But this difficulty is always removed by the examination of other planes.

When the crystal unit was of indeterminate size it was not a very important conception. But the case is very different when the number of molecules in it has been found. It is then ready to play its part in relation to the properties of the crystal, just as the molecule has played its part in relation to other properties. The unit possesses in full all the properties of the crystal: elastic constants of volume, and of rigidity; electric conductivity; thermal conductivity; dielectric capacity; optical activity and so on; all these things, moreover, are vector quantities, not scalar merely.

It lies before us now to consider the structure of the unit in relation to each of these properties, just as in time past we have considered the structure of the molecule in relation to the limited number of ways in which it possesses the properties of the substance of which it is the unit. In this way, a wide field of research opens out, and the entrance into it is by way of our knowledge of the actual contents of the crystal unit.

Among the innumerable problems that now present themselves we may, this evening, consider those which are concerned especially with the relations between the crystal unit and the molecule: the divisibility of the unit into groups, and the degree of resemblance between the group and the chemical molecule.

We find the most ready illustrations in the case of organic crystals, because the division into groups is so well marked. In an address to the Physical Society a year ago,\* it was shown that the naphthalene unit contained two groups similar or identical with naphthalene molecules; that the same held for anthracene; that  $\alpha$ -naphthol,  $\beta$ -naphthol, acenaphthene, and others were similarly divisible into four. Since that time a number of other organic crystals have been examined and always with the same result: there are generally four molecules in the cell, sometimes two, sometimes one. There are no doubt units with three molecules to the cell, but no tested cases can be quoted as yet from among the organic crystals; in the inorganic, quartz is, of course, a notable example.

It is a very suggestive fact that the number in the cell seems to be closely related to the symmetry of the crystal on the one hand and the probable symmetry of the molecule on the other. In the case of  $\alpha$ -naphthol, for example, the substitution of the hydroxyl group for one of the hydrogen atoms may be expected to have destroyed some of the symmetry previously displayed by the naphthalene molecule. It is natural to associate this with the fact that the unit of  $\alpha$ -naphthol contains four molecules, and the unit of naphthalene contains two; while both possess the same symmetry, that of the monoclinic prismatic class. So, again, two molecules of benzene are built into the crystal unit, and four molecules of benzoic acid. The latter molecule must be the more unsymmetrical; and we find, correspondingly, that even with the extra number of molecules the symmetry of benzoic acid is actually less than in the case of benzene. It is suggested by many observations of this kind that the symmetry of the crystal tends to increase with the number of molecules in the unit and also with the symmetry of the molecule.

\* *Proc. Physical Soc.*, 1921, **34**, Dec.

The point has been studied carefully by Mr. Shearer,\* and he has drawn the conclusion that, provisionally at least, these considerations may be expressed in a definite quantitative form.

For the sake of clearness we may, before attempting to state Shearer's rules, review some of the principles of crystal classification, in especial connexion with the conception of the crystal unit.

Of the thirty-two classes into which crystals are divided according to their symmetry, the first has no planes, axes, or centre of symmetry. The crystal unit contains only one molecule, which itself cannot have any symmetry; if it had, the symmetry would appear in the crystal also. The symmetry of the crystal molecule expresses itself in its relation to its neighbours; if every molecule has, for example, the symmetry due to self-coincidence after reflexion across a plane, the symmetry includes also the modes of relation. This must be true throughout the crystal, and consequently the crystal must have a plane of symmetry.

The second class of crystals is distinguished by the possession of a centre of symmetry. If the molecules of which the crystal is composed are themselves asymmetric, it will be necessary to take two of them and arrange them so that they have a common centre of symmetry in order that the unit which contains the two shall also possess a centre of symmetry.

With two similar asymmetric molecules we can also obtain the symmetry of yet two other classes. In one of these, the second molecule becomes similar to the first in regard to the mutual orientation of its parts if it is rotated about some axis through two right angles. The crystal then belongs to the monoclinic sphenoidal class, the name given to it being descriptive of the form which the crystal assumes. The form is simply a consequence of the existence of two molecules in the unit, one being the diagonal of the other.

The remaining two-molecule class has a plane of symmetry. One of the asymmetric molecules, after reflexion across the plane, becomes similar to the other in respect to the mutual orientation of its parts. The molecules are related to one another as right hand to left. This is the monoclinic domal class.

The symmetry of the three two-molecule classes might, of course, be achieved by the use of one molecule only, if that molecule itself possessed the proper symmetry.

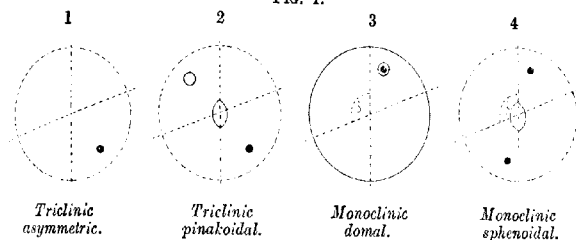
Crystallographers have adopted a very convenient and complete way of representing the properties of crystal classes by diagram. The diagrams of the single molecule and the two-molecule

\* Paper read before the Physical Society of London on December 8th, 1932.

crystals, which we have just described, are shown in Fig. 1. The dot in the figure represents, in our present description, a single asymmetric molecule; in this way we give it more significance than is usual. The molecule represented by a dot is above the plane of the paper, the molecule represented by a small circle is below. It is easily seen that there are no more combinations of the two molecules than those which are shown. We now go on to consider the symmetry of the unit which contains four molecules. Naturally, the symmetry is of a higher order.

If we take a molecule, *A*, and a second, *B*, which is the reflexion of *A* across a plane, and also two, *C* and *D*, which are derived from *A* and *B* by rotation through two right angles about an axis perpendicular to the plane of reflexion, we obtain a crystal which has a plane of symmetry and a digonal axis perpendicular to it. This is the monoclinic prismatic class to which the majority of organic crystals belong.

FIG. 1.



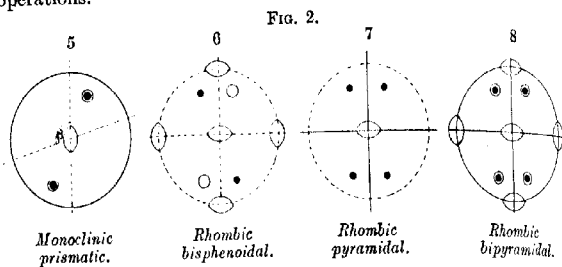
Another four-molecule class is the rhombic bisphenoidal, in which the first and second molecules become mutually coincident after rotation about a digonal axis; and the third and fourth are derived from the first and second by rotation about a second digonal axis perpendicular to the first axis.

In another four-molecule class, the rhombic pyramidal, the second molecule is the reflexion of the first across a plane, whilst the third and fourth are the reflexion of the first and second across a second plane which is perpendicular to the first plane.

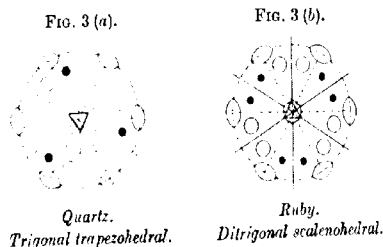
Eight asymmetric molecules are required for the rhombic bipyramidal class. One molecule is reflected across a plane; the third and fourth are derived from the first and second by reflexion across a plane which is at right angles to the first plane; the other four are derived from the first four by reflexion across a plane which is at right angles to both the other planes of reflexion.

The diagrammatic representation of this second set of crystal classes is shown in Fig. 2. These with the other four make up

the eight different classes, built of asymmetric molecules, in which any two molecules can be brought to coincidence after reflexion through a centre of symmetry or reflexion across a plane of symmetry or a digonal rotation about an axis or some combination of these operations.



In this manner we may work our way through all the thirty-two classes of the crystallographer. The remaining twenty-four contain always a tetragonal or trigonal axis. For example, the symmetry of quartz is represented in Fig. 3 (a); if the result were attained by using asymmetric molecules in the construction, the crystal unit would contain six of them. The symmetry of corundum (or ruby or sapphire) [Fig. 3 (b)] would require twelve.



We see that in every case the symmetry can be attained by the use of a proper number of asymmetric molecules. Let us call this the "symmetry number."

Shearer's rules may now be stated as follows:

The number obtained by dividing the weight of the crystal unit by the molecular weight is either equal to the symmetry number or is a sub-multiple of it.

In the latter case, the number obtained by dividing the symmetry number by the number of molecules is the symmetry number of the molecule.

The first of these rules amounts to saying that the chemical molecule, in substance, if not in form, is the basis of construction of the unit. In no case have we found, as yet, that the number of such molecules is greater than the symmetry number. We have often found that it is smaller.

The great majority of organic crystals are monoclinic prismatic; the symmetry number is four, and we find four molecules in the cell. This ought to be the case if the molecule has no symmetry. For instance, there are, in all probability, four molecules in each of the crystals in Table I. We have only tested

TABLE I.

<i>Dihydroxybenzenes.</i>			
	1 : 2. 4 molecules.	1 : 3. 4 molecules.	1 : 4. 4 molecules.
<i>a</i>	11.05	9.56	13.55
<i>b</i>	6.88	10.5	5.22
<i>c</i>	7.05	5.68	8.13
$\beta$	95° 15'	90°	107°
<i>Dinitrobenzenes.</i>			
	1 : 2.	1 : 3.	1 : 4.
<i>a</i>	7.95	10.52	14.1
<i>b</i>	13.0	11.15	6.93
<i>c</i>	7.45	6.07	7.23
$\beta$	112° 7'	90°	92° 18'
<i>Hydroxybenzoic Acids.</i>			
	1 : 2.	1 : 3.	1 : 4.
<i>a</i>	11.56	6.31	10.1
<i>b</i>	11.22	9.03	4.15
<i>c</i>	4.93	11.03	18.27
$\beta$	91° 22'	90°	126° 42'

three of them as yet, namely, salicylic acid, resorcinol, and 1 : 2-dinitrobenzene; these are sure to carry with them the other 1 : 2 and 1 : 3 substances; we may reasonably expect the 1 : 4 substances to contain four molecules also. The 1 : 4-dihydroxybenzene included in the table is the metastable form. The whole set is at present under investigation.

Let us now consider the experimental evidence, and in the first place let us consider how we should expect the X-ray measurements to show up the division of the unit into molecules, and the symmetry relations of the molecules.

The relative positions of the molecules in the unit must, if our ideas are correct, be governed by certain relations :

(a) If a unit contains two molecules one of which is the reflexion of the other across a plane of symmetry, and if we suppose the crystal unit to be so placed that each corner of it is occupied by a representative of one of the two types of molecule, then the



molecule of the other type must lie on a line perpendicular to the plane of reflexion and passing through the centre of one of the faces of the cell.

For, suppose that the figure (Fig. 4) represents a view along the  $a$  axis of the unit: and that, according to convention, the plane of symmetry is perpendicular to the  $b$  axis,  $Ob$ . "A" molecules, represented by arrows, are placed at  $Obdc$ : the end of the arrow in each case lies exactly at a corner of the rectangle. The "B" molecules are the reflexions of the A's across some line parallel to  $Oc$ ; as, for example, the dotted line. As far as symmetry goes, there is no reason why the dotted line should occupy any particular position, so long as it is parallel to  $Oc$ . The actual

FIG. 4.

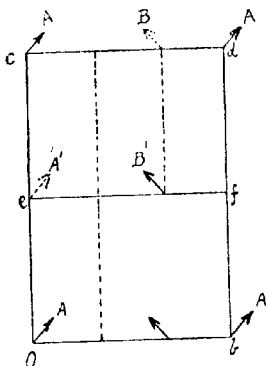
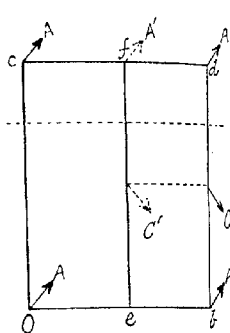


FIG. 5.



position, carrying with it the relative dispositions of A and B, must depend on the forms of the molecules and their mutual reactions.

But further, and this is an important point, the end of the B arrow need not lie on  $cd$  at all; it may lie on  $ef$ , as at  $B'$ , provided that  $ef$  is parallel to  $Ob$  and passes through the middle point of the  $Obdc$  face. The possession of a plane of symmetry by the crystal is ensured if the following operation is successful. Let the molecules, A's as well as B's, be reflected across a plane and the whole afterwards undergo a shift during which the orientation is not altered: the crystal must then be brought to self-coincidence. Now, if the molecule at A is reflected to B and then shifted to  $B'$ , the same operation also reflects  $B'$  to A' and then brings it to coincidence with the A molecule at O. This is satisfactory self-coincidence.

Certain other positions of the B molecule are possible; the shift

being varied so that the double operation brings the  $A$  molecule at  $c$  to coincidence with the  $A$  molecule at some other point than  $c$ . If these be considered in turn, it will be found that they are all covered by the relation (a).

The second relation is as follows :

(b) If a unit contains two molecules, one of which can be brought to coincidence with the other by a digonal rotation about an axis—the crystal then necessarily possesses a principal plane perpendicular to the axis—and if we suppose the crystal unit to be so placed that each corner of it is occupied by one of the two types of molecule, then the molecules of the other type must lie on planes, perpendicular to the axis, which either contain  $A$  molecules, or exactly interleave planes containing  $A$  molecules; or in other words, on planes perpendicular to the axis and passing through a face centre.

If, for example, a digonal rotation about the dotted line (Fig. 5) as axis brings the  $A$  molecule at  $d$  to coincidence with a  $C$  molecule as drawn, the end of the  $C$  arrow may lie on  $bd$ . But it may also lie on  $ef$ ,  $ef$  being parallel to  $Oc$  and passing through the centre of the face  $Odbc$ . The operation that brings the  $A$  molecule at  $d$  to  $C$ , and then to  $C'$ , brings  $C'$  to  $A'$  and then to coincidence with the  $A$  molecule at  $c$ . Thus the whole unit still has digonal symmetry. The figure is drawn for the case when the axis lies somewhere in the plane of the paper; the condition is not necessary, and therefore the position of the molecule at  $C$  or  $C'$ , defined by the end of the arrow, may be anywhere on a plane, perpendicular to the axis, passing through  $bd$ , or  $ef$ , or  $Oc$ .

We should expect to find in the X-ray observations some evidence of the existence of these conditions regarding the relative positions of the different molecules in the crystal unit; and this turns out to be the case. It is to be remembered that the X-ray analysis determines the distance between any plane and the nearest parallel plane which is identical with the former in regard to its relations to the crystal structure. If there are four molecules in the unit, all four are, in general, differently related to any plane in the crystal. We might imagine, for example, that we are considering the spacing between planes which are perpendicular to the plane of the paper and intersect it in lines parallel to  $PP$  (Fig. 6). The four types of molecule will generally project on to the paper in different forms, in a manner roughly indicated by the varieties of the sizes and directions of the arrows  $A, B, C, D$ . The spacing is the distance from  $PP$  to  $QQ$  or  $QQ$  to  $RR$ , because the  $QQ$  plane is the nearest plane to  $PP$  which is indistinguishable from  $PP$ . The magnitude of the spacing is not affected by the presence of  $B, C$ , and  $D$ . This

is the usual case; and if we calculate the spacings of the various planes from the dimensions of the crystal unit, on the supposition that there is only one type of molecule *A*, one of them at each corner of the unit, we must observe values in agreement with those calculated.

But this is not always the case, and it is the exceptions that are important. Consider, for example, the (010) plane, which is perpendicular to the *b* axis, *PQR* (Fig. 7). We have seen that the plane of the digonal molecule *C* may exactly interleave the planes of the *A* molecules. So far as reflexion by the (010) plane is concerned, the effect of the digonal molecules is exactly the same as that of the originals. As shown in the diagram (Fig. 7), they are different to the eye; but the phases of the different parts of the molecules

FIG. 6.

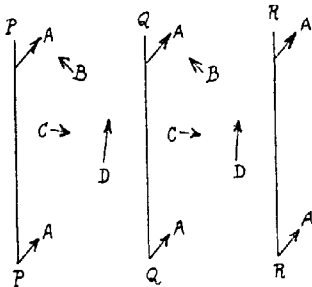
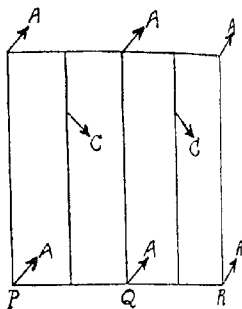


FIG. 7.



are the same, since they can be measured from the projections of the molecules on the line *PQR*. The consequence is that the (010) spacing is exactly halved, as in naphthalene or benzoic acid. If the digonal molecule lies, in the alternative case, in the same plane as the original, the spacing is not altered, as in  $\alpha$ - or  $\beta$ -naphthol.

Again, consider any of the series of planes passing through the *b* axis, or, in other words, the planes of the (010) zone, having the designation (*m*, 0, *n*). If we look along the axis, we cannot tell the difference between a molecule and its reflexion across the plane of symmetry. Let the figure (Fig. 8) represent a section of the unit perpendicular to the (*b*) axis, that is, to the axis of the crystal, so that all lines through *O* are projections of the various planes of the (010) zone. The projection of the molecule *B* is either at a corner of the rhombus, or the middle of an edge, or the middle of the face; this being the consequence of the condition (*a*) above. If, for example, it is at the centre of the face as indicated in the figure, the spacings of the planes *Oc* or *Oa*, that is, (100) and (001),

are halved, but not the spacing of (101), *Og*. It can be shown that in the general case the spacing of the plane (*l*, *O*, *n*) is halved if *l* or *n* is even: but not if both are odd. If *B* is at the middle of *Oa*, the spacings of the planes are halved unless *l* is even: and if it bisects *Oc*, unless *n* is even.

In all these cases the spacings of half the planes are halved. If *B* coincides with *A* as regards its projection on the plane of the paper, no spacing is halved.

When there are four molecules, the same considerations hold, because we can divide the four into two pairs. We can say that *A* and *B* are the diagonal of *C* and *D*, so that it becomes important to find out whether the (010) spacing is halved; and also that *A* and *C* are the reflexion of *B* and *D*, so that we must find out whether spacings of half the planes in the 010 zone are halved, and if so which half.

We can now consider some examples. We may take benzoic acid first.

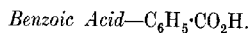


TABLE II.

Zone about 110 Axis.

Plane.	Intensity.		Spacing	Plane.	Intensity.	Spacing
	1st order.	2nd order.	obs.			obs.
118	170	—	—	11 $\bar{1}$	15	3.74
117	33	—	2.30	11 $\bar{2}$	15	3.63
116	20	—	2.50	113	?	3.42
115	320	—	2.72	11 $\bar{4}$	50	3.21
114	380	—	2.97	11 $\bar{5}$	35	2.97
113	440	80	3.21	116	10?	2.72
112	40	—	3.42	11 $\bar{7}$	50	2.50
111	40	—	3.63	11 $\bar{8}$	0	2.30
110	70	—	3.74			

TABLE III.

Zone about "a" Axis.

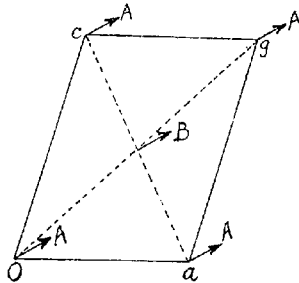
010	0	60	5.16
011	50	30	4.99
012	80	90	4.63
013	100	—	4.19
014	360	25	3.73
015	110	—	3.32
016	120	—	2.97
017	30	—	2.67
018	80	30	2.40

TABLE IV.

Zone about "b" Axis.

106	30	0	2.88
104	90	trace	3.65
102	160	0	4.65
100	200	0	5.45
10 $\bar{2}$	380	120	5.16
104	0	0	—
10 $\bar{6}$	0	0	—

FIG. 8.



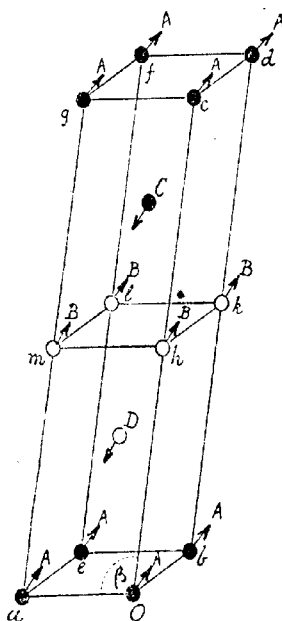
## Reflexions from Cleavage Plane (001).

TABLE V.

	Spacing.	21.6.	
001	0	009	0
002	280	00(10)	30
003	0	00(11)	0
004	220	00(12)	30
005	0	00(13)	0
006	40	00(14)	—
007	0	00(15)	—
008	100	00(16)	Small

In Table II are shown the results of the examination of a long series of planes passing through the (110) zone; they neither contain nor are perpendicular to the axis of the crystal. The

FIG. 9.



$$Oa = 5.44; Ob = 5.18; Oc = 21.6;$$

$$\beta = 97^{\circ} 5'.$$

100 zone, one of which is (010).

over, the spacings of the planes show, from the strength of the second-order reflexion, that the

axis of the zone is  $ab$  in Fig. 9; and Fig. 10 shows some of the planes of the zone, the axis being perpendicular to the plane of the paper. We should therefore expect to find the observed spacings to agree with the calculated; there should be no cases of halving. This is actually the case; the great majority of the planes give easily readable reflexions, some of them very large, and the measurements of the spacings are correct to  $\frac{1}{2}$  or 1 per cent. We may say that the spacings are determined by one set of molecules alone; if we put 4 molecules at the corners of the crystal unit, the positions of the B, C, D molecules are immaterial so far as the actual values of the spacings are concerned.

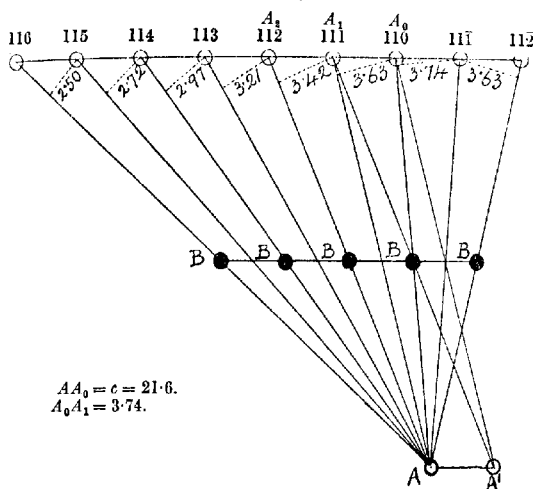
Table III contains the values for the planes belonging to the

This spacing is halved; moreover, the spacings of the planes show, from the strength of the second-order reflexion, that the

actually halved (010) are tending to halve the (011) and (012) also.

Table IV contains the values for the planes belonging to the 010 zone. The planes 102, 104, 102̄, etc., alone show the proper spacings: the 101, 103 show no reflexion when set to the X-rays as if they had the proper spacing. The series of planes is shown

FIG. 10.



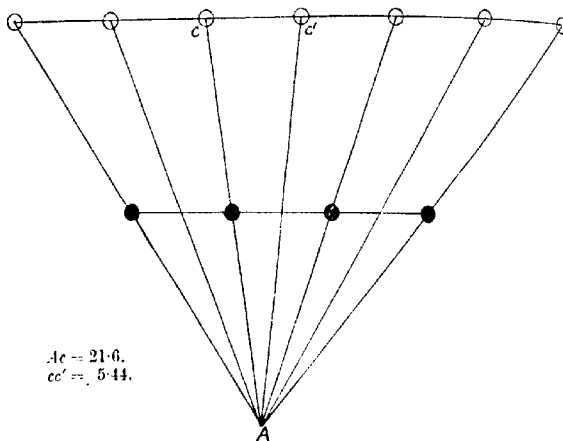
Some of the planes belonging to the (110) zone; that is, to the series of planes passing through *a* and *b* in Fig. 9. The molecules represented by the empty circles differ from those represented by full circles with respect to this series of planes. Consequently, none of the spacings are halved, even although there might be *B* molecules as shown in the figure. In Fig. 9, the reflected molecule must lie on *hk* and *lm* and is placed, provisionally, at *h*, *k*, *l*, *m*. The positions marked *B* in Fig. 10 are then chosen to correspond with the positions of the *B* molecules in Fig. 9. If in respect to the planes shown in Fig. 10 they were exactly equivalent to the *A* molecules, half the spacings would be halved. For instance, the two (111) planes, *A*<sub>1</sub> and *A*'<sub>1</sub>, have a *B* molecule half way between them: the two (112) planes, *A*<sub>2</sub> and *A*'<sub>2</sub>, have not.

in Fig. 11. Some of them show a reflexion for the half spacing; generally a weak one. We conclude that the molecule *B*, looked on as the reflexion of *A*, bisects the line *Oc*. This is also shown in Table V, by the observed values of the intensities of the various orders of reflexion of the 001 plane. All the odd orders are missing. The relative intensities of the fourth and especially the eighth orders may be taken to mean that the positions of the *C* and *D* molecules are approximately as shown in Fig. 9. It is not con-

venient to follow up the structure further, the main point being already clear; but it may be observed that we can conclude the existence of double layers parallel to the 001 or cleavage plane. The members of the double layer present their carboxyl groups towards one another; but the junction of layer to layer is through the hydrogen atoms.

Let us take resorcinol as another example of a four-molecule unit. In this case there are two planes of symmetry at right angles to one another. We may readily show that in this case, if the  $A$  molecule is put at the corner of the unit, a molecule,  $A_x$ ,

FIG. 11.



Planes belonging to the (010) zone. In this case, half the spacings are actually halved, because in this zone the two sorts of molecules are indistinguishable, and they both lie on one half of the planes, and in respect to the other half they interleave each other.

which is the reflexion of  $A$  across a plane parallel to the (100) plane, must lie on a line parallel to the axis of  $x$  and passing through the middle point of a face. Also, because its projection on the (100) plane is indistinguishable from the projection of the  $A$  molecule on the same plane, it follows on the same lines as before that there is a halving of the spacings of half the planes in the 100 zone. The results of Table VI show that this is so, and that the projection of  $A_x$  on the (100) plane is at the centre of the 100 face. So also the results show that the projection of  $A_y$  on the (010) plane is at the centre of the 010 face. This follows from the fact that in both the  $a$  and the  $b$  zones the only planes which show a

reflexion at the calculated angles are those for which two of the indices are odd (see previous discussions of Fig. 8).

TABLE VI.

*Resorcinol.*  $C_6H_4(OH)_2$ .

Rhombic pyramidal: 4 molecules:  $a = 9.56, b = 10.25, c = 5.64$ .

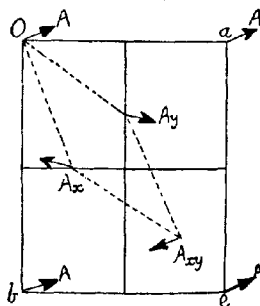
Observed. Calculated.

<i>a zone:</i>	001	$d = 2.84$	5.64
	031	2.98	2.98
	051	1.95	1.97
	010	2.55	10.25
<i>b zone:</i>	100	2.40	9.56
	501	1.82	1.82
	301	2.78	2.78
	101	4.86	4.87—Strong
	103	1.82	1.85
	001	2.84	5.62
<i>c zone:</i>	100	2.40	9.56
	210	4.35	4.35
	110	3.49	7.07—Strong
	120	4.62	4.60—Very strong
	130	1.67	3.29
	140	2.58	2.53
	010	2.55	10.25

If the projections of the four molecules (the fourth is denoted by  $A_{xy}$ ) on the 001 plane are approximately as shown in the diagram (Fig. 12), we realise these conditions and possibly account for certain other striking features in the results, for example, that the (100) and (010) spacings are nearly quartered. The  $A$  and  $A_{xy}$  molecules lie together in planes: the  $A_x$  and  $A_y$  molecules lie in planes which exactly interleave the others.

When the number of molecules in the unit is less than the symmetry number, it is generally possible to draw conclusions regarding the symmetry which the molecule possesses according to Shearer's rules. The naphthalene unit contains two molecules, and its symmetry number is four. Consequently, the naphthalene molecule has a symmetry number two; it possesses twofold symmetry and no more. Although this statement applies to the crystal molecule only, and might be untrue of the chemical molecule, yet, if so, there must

FIG. 12.





be some character in the compound  $C_{10}H_8$  which disposes it to one or other of the two forms according to circumstances.

We can draw also some conclusions regarding the nature of the symmetry of the crystal molecule of naphthalene from the X-ray observations. The molecule must have either a plane of symmetry, a centre of symmetry, or a digonal axis. If it had the first, the second molecule must be the digonal of the first, in order that the crystal which acquires its plane of symmetry from the molecule may acquire its digonal symmetry from the crystal structure. In this case, the (010) plane must be halved; but there is no reason, due to the same condition, why half the planes through the (010) zone should be halved. On the other hand, if the molecule has digonal symmetry and the plane of symmetry is due to structure, half the planes of the (010) zone may be halved, but there is no reason for halving the (010) plane.

FIG. 13 (a).

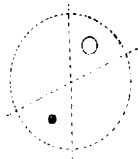
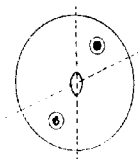


FIG. 13 (b).



It is possible that the molecule has a centre of symmetry. In that case, the *B* molecule is both the reflexion and the digonal of *A*. This may be seen from the diagram. If the symmetry of the molecule is represented by Fig. 13 (a), the monoclinic prismatic symmetry of Fig. 13 (b) can be derived from that of (a), either by reflexion across the plane of the paper or by digonal rotation as indicated. It can then be shown that the planes perpendicular to the axis, which contain the centres of symmetry of *B* molecules, must contain *A* molecules also, or exactly interleave planes containing *A* molecules, and that, at the same time, the centre of symmetry of the *B* molecule must lie on a line parallel to the axis and passing through the centre of one of the faces of the crystal unit. Consequently, we may find that the (010) spacing is halved and also the spacings of half the planes in the (010) zone.

The experimental data are at present insufficient for a definite decision. The measurements on naphthalene were made some time ago and are in need of repetition and additions if they are to be used to settle the symmetry of the molecule. So far as they go, they seem to indicate that the twofold symmetry which the crystal

molecule possesses is due to the existence of a centre of symmetry.\* Probably the same may be said of anthracene, although the available measurements are much less numerous than in the case of naphthalene.

The case of benzene is of great interest. The symmetry number of the crystal is eight, because it belongs to the rhombic bipyramidal class, the last of the eight classes described above. There are only two molecules in the unit. Each molecule has, therefore, a fourfold symmetry of its own. It has *not* got a trigonal axis; still less a hexagonal axis. The conventional method of representing the molecule as a hexagon cannot be taken as a true description of the molecule in the crystal.

FIG. 14 (a).



FIG. 14 (b).

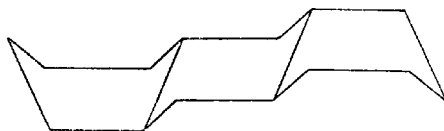


FIG. 14 (c).

Diagrammatic forms of (a) benzene, (b) naphthalene, (c) anthracene, which, respectively, have the symmetries of the crystal molecules, and at the same time show bonds inclined to one another at the tetrahedral angle. The figures are drawn as they would be seen in perspective. The sides of each hexagon are all equal, but do not lie in one plane. The angle between any pair of adjacent sides is the tetrahedral angle,  $109^{\circ} 24'$ . These figures are intended only to show a solution which would be in agreement with the X-ray analysis so far as it has gone.

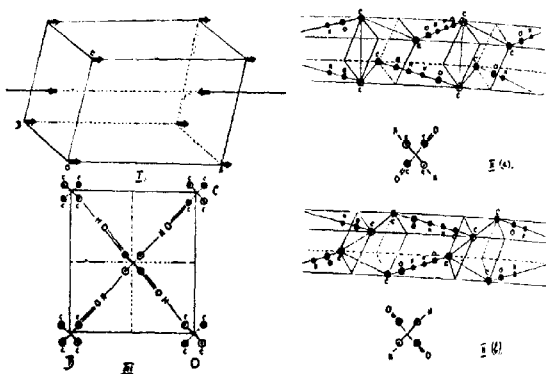
There are not enough experiments to decide the exact symmetry of the crystal molecule of benzene itself; it might be described as the symmetry of any one of classes 5, 6, or 7 (Fig. 2). In the paper on "Organic Crystals" to which reference has been made, it was assumed provisionally that the ring in the crystal would be exactly of the form in which sixfold arrangements of carbon atoms appear in the diamond. A slight modification is shown in Fig. 14 (a), which would not really affect any of the work previously described, and which maintains the tetrahedral orientation of bonds. It has the right amount of symmetry for the crystal molecule of benzene. A combination of two such rings (Fig. 14 b) has a centre of symmetry only, which, as we have said, is probably

\* Note added later.—This is confirmed by further experiment.

the full extent of the symmetry of the crystal molecule of naphthalene. If a third ring of the diamond form is inserted between the latter two, we have an arrangement of three (Fig. 14c) possessing, probably, the symmetry of anthracene. These last considerations are speculative, and are intended merely to show in what directions we must look for results. The questions may be definitely answered by further experiment.

We may take tartaric acid as an example of a crystal of two-fold symmetry. The structure has recently been determined by

FIG. 15.

— TARTARIC ACID. —  $\text{C}_2\text{H}_4(\text{COOH})_2$  —

- I. Crystal unit of tartaric acid and arrangement of molecules.
- II. (a) and (b). Enantiomorphous forms each showing the arrangement of two molecules along the axis of  $a$ , and the projection of the carbon core of the molecule on a plane perpendicular to the  $a$  axis.
- III. Section of the unit perpendicular to the  $a$  axis showing the relative arrangement of the molecule (at each corner) and its digonal (at the centre).

Mr. Astbury.\* The unit contains two molecules, and each must therefore be asymmetric. The molecule could not in any case have a plane of symmetry, because its optical activity implies the existence of something of a spiral nature in the structure of the crystal; and a right-handed spiral becomes a left-handed spiral by reflexion. An active crystal cannot contain equal amounts of opposite spiralities. The crystal cannot possess a plane of symmetry for the same reason that the molecule cannot. Of the two molecules, one must be the digonal of the other, and it is found that the (010) spacing is halved. The structure is illustrated in Fig. 15. It shows, perhaps unexpectedly, two spirals. One of them is

\* Paper read before the Royal Society on December 7th, 1922.

right-handed, one left, but they are not the mirror images of one another, occurring as they do in different parts of the crystal structure. The screw which is found in the carbon atoms at the centre of the molecule is in all probability permanent, and is the cause of the activity of tartaric acid in solution. The other screw is found in the hydroxyl groups, and may be expected to appear in the crystal only, where it compensates the first screw structurally. When the crystalline bonds are dissolved, the second screw disappears. Its effect on light is opposite to that of the first, and we must assume is greater; so that tartaric acid may revolve the plane of polarisation in one direction as a crystal and in the other direction when in solution.

FIG. 16.

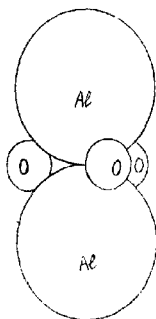
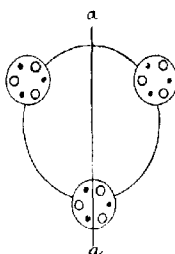


FIG. 17.

FIG. 16. Arrangement of atoms in  $\text{Al}_2\text{O}_3$  molecule.FIG. 17. Section through centre of  $\text{Al}_2\text{O}_3$  molecule, perpendicular to the axis: showing, diagrammatically, a possible arrangement of the electrons in the oxygen atoms, which gives the proper symmetry to the molecule.

The quartz crystal has sixfold symmetry, and the unit contains three molecules. These are arranged spirally ("X-Rays and Crystal Structure," p. 165) so that the trigonal symmetry is due to the structural arrangement. According to Shearer's rule, each crystal molecule has, therefore, a twofold symmetry and no more. The crystal has digonal axes, and it follows that each molecule has digonal symmetry.

Corundum (ruby or sapphire) has twelvefold symmetry. There are two molecules in the unit, which has not quite the form defined by the crystallographer's ratio  $a:c = 1:1.365$ . It is necessary to double the  $c$  axis, making the ratio  $1:2.73$ . The unit then contains two molecules. According to Shearer's rule, the molecule has, therefore, sixfold symmetry. The ruby structure has been solved, and it is found that the molecule  $\text{Al}_2\text{O}_3$  is built into

the structure in the form shown by the figure (Fig. 16). The trigonal symmetry is obvious; but the nature of the twofold symmetry which must also be there is not so clearly shown by the form of the molecule. The question is answered by considering the position of the molecule in the crystal. It then appears that the molecule has no plane of symmetry (see "X-Rays and Crystal Structure," new edition, in the press); it possesses a digonal axis, namely,  $aa$  in the figure. In this case, then, the molecule contributes the trigonal and digonal axes, and the planes of symmetry are due to the structure. It may be well to point out that a trigonal axis with one plane of symmetry through it gives sixfold symmetry; and although there are necessarily three such planes of symmetry if there is one, the symmetry number is not raised in consequence.

It is not really surprising that the  $Al_2O_3$  molecule has no plane of symmetry. Possibly the six electrons in the outer oxygen shell are so arranged as to give the atom the symmetry which is represented in the usual way by the dots and small circles of Fig. 17; the molecule then has a digonal axis but no planes of symmetry.

The preceding examples will serve to illustrate the nature of the relations between the crystal unit and the crystal molecule. There still remains the relation between the crystal molecule and the chemical molecule. So far, experiment shows that there is often a very close resemblance, but further experience is required to show how close it is. Further experience is also required before we can answer the very important question, To what extent can the properties of the one be deduced from the properties of the other? A very wide field of research is opening out; there is no need to attempt too much in the way of deduction and generalisation until it has been more fully explored.

In conclusion, may we make a request? It is often difficult to obtain crystals suitable for examination. Crystals can be handled in the form of fine powder, and sometimes no other course is possible. But the method of the ionisation spectrometer is more convenient and exact. The combination of the two methods is the best of all. For use with the spectrometer, the crystal should weigh a few milligrams at least, and should be of uniform composition, although it need not show any definite form. Very large numbers of crystals which would repay analysis are described in works on crystallography. Very few are easily obtainable; mainly, one supposes, because their usefulness was imagined to be complete when the outer form had been described. It may be that crystals which would be of great use are to be found in small quantities here and there, in museums or laboratories or works. The simpler derivatives of benzene and naphthalene are examples. Sometimes

an isolated crystal of good structure forms accidentally. The crystal of benzoic acid the measurements of which have been described was found by Dr. Brady in a bottle of benzaldehyde which had been standing undisturbed for more than a year, and many other specimens have been given us in the same kind way. We should be grateful for the loan or gift of still more specimens of this nature.

### CCCXXXIII.—*The Purification of Methyl Alcohol by means of Sodium Hypochlorite.*

By ROBERT CHARLES MENZIES.

By the established technical methods, there is no difficulty in obtaining from crude wood spirit methyl alcohol containing only 2 per cent. of acetone; but this is sufficient to render the alcohol useless for many purposes. Complete separation by fractionation is slow and expensive.

The reaction between hypochlorites and acetone according to the equation  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + 3\text{MOCl} \rightarrow \text{CHCl}_3 + \text{CH}_3\cdot\text{CO}_2\text{M} + 2\text{MOH}$  has been used for the removal of acetone from methyl alcohol, but working instructions have not been given. By the method described below, pure methyl alcohol can be obtained from mixtures containing up to 12 per cent. of acetone, and it is now established as a routine process in this laboratory.

Preliminary experiments showed that sodium hypochlorite attacks acetone preferentially to methyl alcohol; the action begins in the cold, taking place almost instantaneously with evolution of much heat. There is also above  $50^\circ$  a vigorous action between methyl alcohol and sodium hypochlorite, which, however, occurs at the ordinary temperature only to a limited extent. The conditions determining the latter action are quite definite and can be easily avoided.

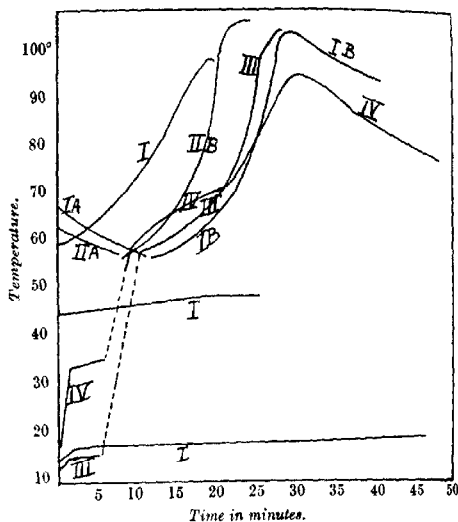
#### *Preliminary Experiments.*

In the following experiments 50 c.c. of a strongly alkaline hypochlorite solution containing 159 grams of available chlorine per litre were mixed with 25 c.c. of water and 5 c.c. of the alcohol; the constituents were mixed in a vacuum flask, and temperature-time curves plotted.

Curve I for pure methyl alcohol (99.8 per cent.), free from acetone, shows at  $15^\circ$  a rise of about  $2.5^\circ$  in the first two minutes, followed by a slow rise to  $21.5^\circ$  after three and a half hours (only partly shown). After heating to  $45^\circ$ , there was a further rise of  $4^\circ$  in twenty-five minutes. After heating to  $60^\circ$ , a vigorous reaction

set in and the curve slopes steeply upwards; the rise in temperature was arrested at  $98.5^{\circ}$ , when gentle boiling commenced.

Since sodium hypochlorite changes exothermically into a mixture of chlorate and chloride, the question arose whether the slope of the curve obtained on adding alcohol to sodium hypochlorite was in any way due to this self-oxidation and reduction of the hypochlorite. In experiment No. 1A, the mixture of water and hypochlorite was therefore first heated to  $68^{\circ}$  without addition of alcohol; the mixture at once began to cool, the temperature falling  $10^{\circ}$  in ten minutes. Five c.c. of methyl alcohol were then added. After



a preliminary cooling of  $1^{\circ}$ , owing to the alcohol having been added cold, the temperature rose rapidly as shown in IB. This curve is similar to, but steeper in slope than curve I, probably because the reaction had been partly completed at lower temperatures in the earlier experiment.

Curves IIA and IIB differ from IA and IB only in that a fraction of alcohol was used which boiled  $0.2^{\circ}$  lower; both samples were free from acetone.

Curve III was for a commercial "pure methyl alcohol" containing 0.5 per cent. of acetone. The initial rise from  $13^{\circ}$  to  $15^{\circ}$  is as in curve I; the behaviour of the mixture after heating to  $55^{\circ}$  is practically identical with that of IB.

These experiments show that the slope of the curve for the purer samples of methyl alcohol is characteristic. Curve IV, for a "methylic alcohol" containing 11.6 per cent. (or a total of 0.58 gram) of acetone, shows at 17° a rise of 15.5° within two minutes and a further rise of 2.5° in the next four minutes. The mixture was then heated to 55°, when it gave a curve which differed from curves I to III as follows:

(i) The slope of the curve from 60° to 70° was much smaller, probably owing to the distillation of chloroform formed at the commencement of the action.

(ii) The temperature of the mixture never reached 100°, as about 25 per cent. of the hypochlorite taken had already been destroyed by the acetone.

In a duplicate experiment, No. V (not plotted), the hypochlorite solution was mixed with water containing 0.58 gram of acetone, the heat capacity of the mixture being also the same as in curve IV. The temperature rose at once from 18° to 31.5°, or 2° less than in the previous case. This agrees with the facts that the mixture of methyl alcohol and water is exothermic (Bose, *Z. physikal. Chem.*, 1907, 58, 597) and that in experiments I and III an initial rise of 2° was observed. The mixture No. V showed no further rise when heated to 54°, but cooled slowly.

These experiments prove that whilst acetone is attacked instantly by sodium hypochlorite in the cold, methyl alcohol is only slowly attacked unless the temperature is raised above 50°.

Ethyl alcohol and fermentation butyl alcohols are also attacked vigorously by sodium hypochlorite at higher temperatures. In the latter case the mixture must be heated almost to boiling, and, as butyl alcohol is not readily soluble in water, it is necessary to stir; but the mixture continues to boil vigorously for some time after removal of the external source of heat.

Formic acid was detected after reaction between methyl alcohol and sodium hypochlorite. Acetic acid was not tested for in the ethyl alcohol reaction mixture, but on acidifying the butyl alcohol mixture, the smell of butyric acid was at once apparent.

#### *Methods of Analysis.*

Acetone was estimated throughout by Messenger's method (*Ber.*, 1888, 21, 3368). No process of purification of methyl alcohol gave a zero figure by this test; the lowest was 0.03 per cent., but the sample was probably free from acetone, as it gave no smell of iodoform. Artificial solutions containing 0.014 per cent. of acetone gave a cloudiness due to iodoform and the characteristic smell of this compound. The purest samples of methyl alcohol,



therefore, probably contained some substance (or substances) other than acetone which destroys a small amount of sodium hypiodite, including perhaps methyl alcohol itself, in view of its action on the hypochlorite. Gibbs (*Philippine J. Sci.*, 1912, 7, 57) has shown further that methyl alcohol exposed to the joint action of air and sunlight contains formaldehyde. The first runnings from a sample of methyl alcohol where sodium hypochlorite solution had been poured down the fractionating column before beginning the distillation, showed in the first 60 c.c. an apparent acetone content of 0.39 per cent., whilst the next 1350 c.c. showed only 0.077 per cent.; in neither case was any iodoform observed during the analysis.

Total chlorine was estimated by boiling samples with sodium dissolved in ethyl alcohol for about two hours, the chlorine formed being estimated volumetrically. Useful comparative results were obtained, but quantitative accuracy in estimating very small percentages of chlorine is not to be expected. A solution of chloroform in ethyl alcohol made up to contain 0.14 per cent. of chlorine showed by this method 0.11 per cent.

#### *Details of Purification.*

*Experiment VI.*—The crude methyl alcohol used contained 12.08 per cent. (w/v) of acetone; esters (expressed as methyl acetate) 6.7 per cent.;  $d_{4}^{25}$  0.8292. These figures indicate an approximate methyl alcohol content of 600 grams per litre.

The sodium hypochlorite was made up by dissolving 1 kilogram of powdered caustic soda in 4 litres of water and passing in 680 grams of chlorine, being 77 per cent. of the theory. This solution was found to contain 144.7 grams of available chlorine per litre.

Quantitative reaction according to the equation given (p. 2787) requires that 25.34 c.c. of the above solution should remove 1 gram of acetone. 2800 C.c. of the hypochlorite solution (= 110.4 grams of acetone) were now added to 1 litre of the alcohol, containing 120.8 grams of acetone mixed with 2 litres of water. One hundred and three c.c. of chloroform separated, the volume of the brown supernatant liquor being 5700 c.c. The chloroform layer contained 3.5 per cent. of acetone, or 3.6 grams in all, whilst the supernatant liquor contained 0.1015 per cent., or 5.77 grams in all. Thus, of the 120.8 grams of acetone originally present,  $110.4 + 3.6 + 5.77 = 119.77$  grams have been accounted for. This proves that the reaction between sodium hypochlorite and acetone proceeds to completion before that with methyl alcohol begins.

The residual acetone in the brown liquor was removed by 225 c.c. of the hypochlorite solution (equivalent to 8.9 grams of acetone), the addition of which in excess of that sufficient to remove the last trace of acetone was attended by discharge of the brown colour.

METHYL ALCOHOL BY MEANS OF SODIUM HYPOCHLORITE. 2791

This aqueous solution of methyl alcohol was now distilled from a metal still through a Raschig column four feet high.

The fractions obtained are tabulated as follows (Table I).

TABLE I.

No.	Temp.	Volume in c.c.	Weight in grams.	Density.	Acetone equivalent per cent.	Total chlorine per cent.
1	64—67°	50	45.9	0.918	0.17	0.13
2	67—77	75	62.8	0.837	0.11	0.01
3	77—78	100	85.1	0.851	0.085	0.005
4	78—80.4	200	172.1	0.8605	0.063	0.0007
5	80.4—92	200	175	0.875	0.055	0.0002
6	92—98	500	480.1	0.960	0.015	not taken
7	98—100	500	494.7	0.989	0.008	

In the analysis of fraction 1, a cloudiness due to iodoform was noticed; this cloudiness grew fainter with each successive fraction and was just perceptible in the case of No. 4.

After refractionation of Nos. 6 and 7 up to 98°, all the fractions were mixed, and the alcohol was dried by distillation after the addition of a little sulphuric acid and then over sodium, the fractions finally obtained being as follows :

TABLE II.

No.	Temp.	Weight in grams.	Density.	Acetone equivalent per cent.	Total chlorine per cent.
1	63—65°	39.9	0.798	0.04	0.003
2	65.6—66.4	375.1	0.8008	0.063	0.0036
3	66—70	41.9	0.81	0.15	—

From Landolt's tables :

F <sub>1</sub>	contains	99.25	per cent. of methyl alcohol or	39.7	grams.
F <sub>2</sub>	"	98.3	" " "	368.6	"
F <sub>3</sub>	"	95	" " "	39.8	"

Total 448.1 "

As 600 grams of methyl alcohol were present in the litre of crude methyl alcohol, this is a yield of 74.7 per cent.

*Experiment VII.*—In another experiment, 500 c.c. of a sample of commercial methyl alcohol, containing 7.9 grams of acetone per 100 c.c. and 79 per cent. by weight of methyl alcohol, were treated with sodium hypochlorite, the distillate was dried over quicklime, and the following fractions were obtained :

TABLE III.

No.	Temp.	Weight in grams.	Density 0°/0°.	Acetone per cent.	Total chlorine per cent.
1	66.5—69°	203	0.82235	0.116	0.0114
2	69—72	57	0.824 (15.5°)	0.2	0.0085

From Landolt's tables :

F <sub>1</sub>	contains	95.6	per cent. of methyl alcohol or	194	grams.
F <sub>2</sub>	"	90	" " "	51	"

Total 254 " 5 R\* 2

This is a recovery of 74.9 per cent. of the methyl alcohol originally present.

Table IV indicates that subsequent treatment with drying agents alone is required to obtain a very pure product.

TABLE IV.

	"Acetone" per cent.	B.p. corr. to 760 mm.	Density 0°/0°.	Per cent. MeOH from tables.
I. Purified over (1) sulphuric acid, (2 and 3) sodium.	0.05	64.5—64.7°	0.811076	99.67
II. (1) sodium and iodine, (2) sulphuric acid.	0.064	64.6—64.9	0.811043	99.68
III. I and II mixed. Redistilled over sodium and bone charcoal. Middle fraction only.	0.086	64.5—64.7	0.810771	99.78
No iodoform formed during these analyses.				

Sidney Young gives 64.7° as the boiling point of pure methyl alcohol at 760 mm. (T., 1902, 81, 719).

#### *Heat Effect of the Reaction.*

To give an indication of the concentrations of acetone and of sodium hypochlorite which could conveniently be used in technical application of this process, the temperature changes observed in the course of experiment VI are now recorded. As stated, 2800 c.c. of sodium hypochlorite solution containing 14.47 per cent. of available chlorine were added to one litre of crude alcohol (12.08 per cent.), mixed with two litres of water, the mixture thus containing 4.03 per cent. of acetone. Addition of the first 1000 c.c. of hypochlorite was followed by a rise in temperature of 24°; after cooling, addition of the next 1000 c.c. was followed by a rise of 18°; whilst the final 800 c.c. caused a rise of 10.5°. The total rise in temperature was thus 52.5°. This is too great for a large-scale process, as, the concentrations indicated being used, too rapid addition of the sodium hypochlorite causes the chloroform formed to boil vigorously. The acetone content of wood spirit to be treated in large-scale work ought not to exceed 2.5 to 3 per cent., a concentration, as already stated, easily obtained by the use of existing technical methods. In experiment VII, the alcohol was diluted with water to an acetone content of 2 per cent. The sodium hypochlorite was added at one time, and the resulting temperature was not inconveniently high.

The sodium hypochlorite should be added to the alcohol to be purified and not vice versa.

*Summary.*

In the above, a method of removing acetone from crude methyl alcohol by means of sodium hypochlorite has been described. It has been shown that as a laboratory method it is satisfactory, methyl alcohol of a high degree of purity being obtained readily and in good yield.

Since sodium hypochlorite is a liquid and does not attack iron, the method ought to be capable of technical application, and to possess advantages over those making use of calcium hypochlorite and of free chlorine.

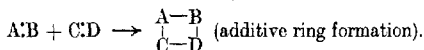
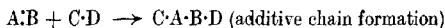
The author wishes to thank Mr. J. W. Armit, B.Sc., for invaluable assistance and to express acknowledgment to the Carnegie Trust for a Fellowship, during the tenure of which this work was carried out.

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CCCCXXIV.—*The Additive Formation of Four-membered Rings. Part I. The Synthesis and Division\* of Derivatives from 1:3-Dimethindiazidine.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT.

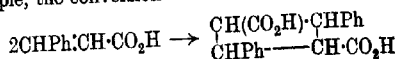
ADDITIVE reactions, considered from the point of view of their mechanism, fall into two main groups, which may be symbolised thus:



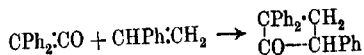
\* The word "division" is used because it is essential to have some word that distinguishes between the cutting of a ring asunder (that is, cutting at two points) and the mere cutting of a ring (at one point), for which process the words "fission" and "scission" are in common use. It is obvious that there is a basic difference between the phenomena, which becomes even more clearly evident if the reverse processes are considered; for in this paper it is shown that the "synthesis" of a four-membered ring by the placing together of two double bonds often proceeds spontaneously at the ordinary temperature, whilst it is recognised that the "closure" of a four-membered ring from a single open-chain molecule is, in general, one of the most difficult operations in ring formation (T., 1921, 119, 951).

The opposite of "division" (parting asunder) is "synthesis" (placing together), and the authors hold the opinion that these terms should be carefully preserved from such as "scission" and "closure" in all discussions on ring formation.

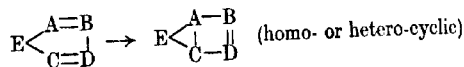
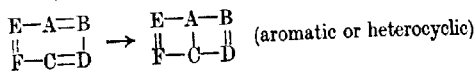
Comparatively little attention has hitherto been directed to the second of these types, the main examples of which have usually fallen within one of the two following special cases,—(a) dimerisation, that is, the special case in which A:B and C:D are identical, as, for example, the conversion of cinnamic acid into truxillic acid:



and (b) reactions of the ketens, for instance, the following formation of triphenylcyclobutanone (Staudinger and Suter, *Ber.*, 1920, 53, 1092):

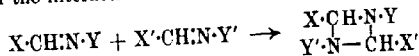


The general type of change to which these instances belong is clearly the intermolecular analogue of the intramolecular four-membered ring transformations by means of which the properties of aromatic and allied heterocyclic compounds have recently been interpreted (this vol., p. 1133):



and therefore it would appear of first importance for the further study of aromatic structure to endeavour to carry the intermolecular phenomenon outside the two specialised fields within which it has hitherto been investigated, and to prove, if possible, that it has a very large degree of generality. It is with this object that the present series of researches has been commenced.

In this paper, it is proposed to examine the conditions of formation, and the stability, of the 1:3-dimethindiazidine ring, the synthesis of which might be expected to follow, in accordance with the general equation for additive ring formation already given, from the interaction of two azomethines:

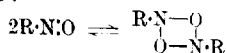


It may be stated at once that the experiments described in this paper clearly demonstrate the occurrence of this reaction, and are mainly concerned with its more exact study.

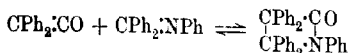
If it is indeed true that the intramolecular transformations previously examined are to be traced to a generally prevailing tendency towards the additive formation of four-membered rings,

which operates whether the participating double bonds are in the same or in different molecules, then it follows inevitably that the intermolecular reactions now under consideration must be reversible.\* Experiment shows that this is the case; but in order to render intelligible the results described in this paper, it is necessary to examine the nature of the evidence in some detail.

First, there is indisputable evidence of reversibility in each of the two special fields within which additive ring formation has hitherto been studied. Thus, as regards dimerisation, the reaction by which truxillic acid is formed is reversed at higher temperatures (Riiber, *Ber.*, 1902, 35, 2908), whilst in the heterocyclic series a good example is provided by the dimerisation of nitroso-compounds, which, in numerous cases, reach measurable equilibria at the ordinary temperature :



Amongst the ketens, there is, for instance, the observation (*loc. cit.*) that triphenylcyclobutanone is resolved into its factors at 200°, and, in the heterocyclic series, an example of reversibility is afforded by the reaction investigated by Staudinger and Göller (*Ber.*, 1911, 44, 532) :



Thus the most cursory examination of the literature reveals unmistakable indications of a uniformity between the reactions under discussion and the intra-annular and benzenoid transformations the basis of which we wish to find in intermolecular phenomena.

We may now adopt the following fundamental hypothesis, the consequences of which will be found to agree in a very satisfactory way with all the observations which have hitherto been made to test it : *In double-bonded compounds there exists a general tendency towards the establishment, in the liquid state or in solution, of an equilibrium with the dimeric form :*

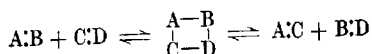


In certain cases the equilibrium might be very one-sided (as with carbonyl and azo-compounds, the molecular weights of which in solution are almost invariably normal), or it might be very slowly attained (as with most ethylenic compounds at the ordinary temperature); but in other cases, for instance, many azomethines,

\* The argument is analogous to that which was recently used (this vol., p. 1765), when it was shown that the basis of three-carbon tautomerism is to be found in the reversibility of Michael's reaction.

nitroso-compounds, and ketens, there is much evidence that no such extreme conditions prevail, and that the above equilibrium may become of a measurable order, and may be rapidly established.

When solutions containing two such equilibrated systems are mixed, new equilibria, corresponding with limited additive ring formation between two unlike molecules, will, in general, be established. Since the cycloid so obtained can, with equal *a priori* probability, undergo division in either of two directions, the new balanced system will be a two-fold one, four products being in equilibrium with the ring compound :



unless the insolubility, infusibility, or volatility of one of the substances, or some property inherent in the cyclic additive product, definitely determines the course of the change.

In a completely equilibrated solution, in addition to the above two-fold equilibrium, there will be four simple equilibria between each of the four double-bonded substances and its dimeride. As a consequence of the hypothesis, three types of result are to be expected on studying a sufficient number of instances. *Case 1.*—If the proportion of cyclic substances at equilibrium is relatively small, so that the isolable forms of the reacting substances are the monomeric forms, and if, also, equilibration is slow, then either the factors ( $A:B + C:D$ ), or the products ( $A:C + B:D$ ), or the intermediate cycloid  $\begin{pmatrix} A-B \\ | \quad | \\ C-D \end{pmatrix}$ , or a mixture of all five might be

obtained on evaporation after a period of time. *Case 2.*—If the proportion of cyclic substances is small at equilibrium, and if equilibration is rapid, then, on evaporation, one should obtain a mixture either of the factors or of the products, according to the manner in which the equilibrium is shifted during evaporation by the deposition from solution of the substance which happens to be the first to crystallise. *Case 3.*—If the dimeric substances are comparatively slightly dissociated, the results, for slow and quick equilibration, would be the same as in cases (1) and (2), excepting that, in rapid equilibration, the intermediate cycloid  $\begin{pmatrix} A-B \\ | \quad | \\ C-D \end{pmatrix}$  might conceivably

be obtained as sole product if it were the first to crystallise.

In many of the examples studied, equilibration took place rapidly at the ordinary temperature; in some cases it proceeded rather slowly; in almost all cases the results proved that the formation of cyclic substances in the equilibrated solution was relatively small, so that the isolation of the intermediate diazidine was

possible only in those instances in which the two successive changes (particularly the second one) proceeded at a small velocity. Of the fifteen instances which have been studied, details of which are given in the experimental portion, five were slow reactions falling within case (1), two were moderately slow reactions which are a little difficult to classify, and eight were rapid reactions falling under case (2). No instance belonging to case (3) has yet been met with in the 1:3-dimethindiazidine series. Thus four types of experiment have been carried out in order to test the consequence of the postulate on p. 2795: (A) Experiments (on slow reactions belonging to case 1) leading to the isolation of the intermediate diazidine by manipulation of the solution while still out of equilibrium, and to the division of the pure cycloid into its products (three experiments). (B) Experiments (also on slow reactions belonging to case 1) leading to the proof that an equilibrium exists between the factors, the cycloid, and the products, and that the same equilibrium can be approached from either side (two experiments). (C) Experiments (on moderately fast, or fast reactions belonging to case 2) leading to the isolation of the two products of division of the cycloid (ten experiments). (D) Experiments (on rapid reactions belonging to case 2) leading to the isolation of the factors in the presence or absence of excess of one of them (three experiments).

These experiments confirm in a remarkable way the consequences, as regards ring formation from azomethines, of the hypothesis introduced on p. 2795. Work has now been commenced with the view of examining its application to the interactions of compounds containing various types of double bond (C=C, C=N, C=O, C=S, N=N, and N=O) with themselves and with one another, and enough has already been done to show that the additive formation of four-membered rings in the sense of the equations given is a process of great generality, and that in all probability we are here dealing with a simplified form of one of the chief types of change which take place within the nuclei of aromatic and heterocyclic substances.

#### EXPERIMENTAL.

(A) *Additive Reactions between Azomethines Leading to 1:3-Dimethindiazidines and the Division of these, yielding Azomethines.*

(I) *The Reaction*  $(p) \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NPh} + \text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Br} (p) \rightleftharpoons$   
 $(p) \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NPh} \rightleftharpoons (p) \text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Br} (p) +$   
 $\text{C}_6\text{H}_4\text{Br}(p) \cdot \text{N} - \text{CHPh}$   
*p-Hydroxybenzylideneaniline was mixed with about*

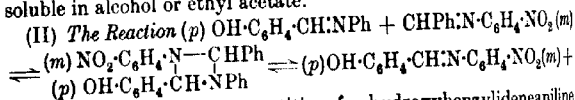


half the quantity of hot alcohol required to dissolve it, and an equivalent of benzylidene-*p*-bromoaniline added. The hydroxy-base at once dissolved and the solution was immediately cooled and evaporated in a vacuum at a low temperature.

*3-p-Bromophenyl-2-p-hydroxyphenyl-1:4-diphenyl-1:3-dimethindiazidine.*—This substance separated from the solution in pale green, glistening leaflets, and was recrystallised from cold alcohol in the same way. It melted at 165–167°, but on keeping for a short time in the fused condition was transformed into the azomethines mentioned below (Found: C = 68.0; H = 4.8; N = 6.4; Br = 17.85.  $C_{26}H_{21}ON_2Br$  requires C = 68.2; H = 4.6; N = 6.1; Br = 17.5 per cent.).

*Division of the Diazidine into p-Hydroxybenzylidene-p-bromoaniline and Benzylideneaniline.*—This reaction takes place when the ring-compound is either fused for a short time or heated in alcohol. The mixture obtained by either method may easily be separated into its constituents by means of benzene, in which the hydroxy-bromo-derivative is insoluble. The latter was identified by analysis (Found: N = 5.2 per cent.) and by direct comparison, and by the melting point of its mixture, with the substance described below. The benzylideneaniline was also identified by similar means (Found: N = 8.1 per cent.).

*p-Hydroxybenzylidene-p-bromoaniline.*—This substance is formed with evolution of heat when *p*-hydroxybenzaldehyde and *p*-bromoaniline are ground together, but it is best prepared by adding one equivalent of *p*-bromoaniline to a boiling saturated solution of *p*-hydroxybenzaldehyde in ethyl alcohol. The precipitate, which rapidly separates from the hot solution, is collected after cooling and crystallised from ethyl acetate, from which the pure base separates in small, pale yellow needles (Found: C = 56.8; H = 3.8; Br = 28.7.  $C_{13}H_{10}ONBr$  requires C = 56.5; H = 5.1; Br = 29.0 per cent.). It is almost insoluble in benzene or ligroin, but easily soluble in alcohol or ethyl acetate.



*CHPh.NPh.*—Equivalent quantities of *p*-hydroxybenzylideneaniline and benzylidene-*m*-nitroaniline were mixed in cold ethyl benzoate solution, and the orange-brown needles which separated on seeding were collected from time to time, until examination by a lens indicated the deposition of a second substance.

*3-m-Nitrophenyl-2-p-hydroxyphenyl-1:4-diphenyl-1:3-dimethindiazidine.*—This substance separated from cold ethyl alcohol in long, felted, orange needles, m. p. 178° with previous sintering (Found:

C = 73.5; H = 5.2.  $C_{26}H_{21}O_3N_2$  requires C = 73.8; H = 5.0 per cent.).

*Division of the Diazidine into p-Hydroxybenzylidene-m-nitroaniline and Benzylideneaniline.*—This was done by the two methods used in the preceding case. The hydroxynitro-base was identified with the substance described below by analysis (Found: N = 12.0 per cent.), by direct comparison, and by the melting point of the mixture. The benzylideneaniline was identified as before (Found: N = 8.0 per cent.).

*p-Hydroxybenzylidene-m-nitroaniline.*—*p*-Hydroxybenzaldehyde and *m*-nitroaniline condense when boiled together in alcoholic solution for twenty-four hours. The product crystallises from alcohol in short, stout needles, m. p. 190–191° (Found: C = 63.7; H = 4.3; N = 11.7.  $C_{13}H_{10}O_3N_2$  requires C = 64.4; H = 4.2; N = 11.6 per cent.). It is almost insoluble in benzene or ligroin, but easily soluble in alcohol or ethyl acetate.

(III) *The Reaction with p-nitrobenzylideneaniline and benzylidene-o-nitroaniline* was carried out like the preceding one, and the cycloid isolated in the same way, excepting that benzene was used in place of ethyl benzoate.

*3-o-Nitrophenyl-2-p-nitrophenyl-1 : 4-diphenyl-1 : 3-dimethindiazidine.*—This substance crystallises from benzene in fine, buff-coloured needles, m. p. 163–165° (Found: C = 68.7; H = 4.6.  $C_{26}H_{20}O_4N_4$  requires C = 69.0; H = 4.4 per cent.).

*Division of the Diazidine into p-Nitrobenzylidene-o-nitroaniline and Benzylideneaniline.*—This decomposition was carried out as in the preceding case, and the products were separated with the aid of ligroin, in which the dinitro-base is sparingly soluble. The latter was identified with the substance described below, and the benzylideneaniline as in the preceding examples.

*p-Nitrobenzylidene-o-nitroaniline.*—This was formed by heating *p*-nitrobenzaldehyde with *o*-nitroaniline without a solvent until water vapour ceased to be evolved. The product was drained on porous porcelain from a little sticky matter, and then recrystallised from benzene, from which it separated in bright yellow very minute needles, m. p. 118° (Found: C = 57.8; H = 3.3.  $C_{13}H_9O_4N_3$  requires C = 57.6; H = 3.3 per cent.).

(B) *Additive Reactions between Azomethines Leading to an Equilibrium which can be Reached from Both Sides.*

(IV) *The Reaction (m)*  $NO_2 \cdot C_6H_4 \cdot CH : NPh + CHPh : N \cdot C_6H_4Br (p) \rightleftharpoons \text{cycloid} \rightleftharpoons (m) NO_2 \cdot C_6H_4 \cdot CH : N \cdot C_6H_4Br (p) + CHPh : NPh$ .—The cycloid was not isolated in this case. Equivalent quantities (a) of *m*-nitrobenzylideneaniline and benzylidene-*p*-bromoaniline, (b) of

*m*-nitrobenzylidene-*p*-bromoaniline and benzylideneaniline, were mixed in benzene solution and kept at 80–100° for several weeks and then examined. Identical results were obtained in both cases. A quantity of *m*-nitrobenzylidene-*p*-bromoaniline (below) separated when the solvent was evaporated and the residue rubbed with a little fresh benzene. *m*-Nitrobenzylideneaniline was obtained by tituration with cold ligroin, which on evaporation deposited benzylidene-*p*-bromoaniline. Benzylideneaniline was obtained from the ultimate residue by rubbing with carbon disulphide. The four products were identified by direct comparison with authentic specimens, and by the melting points of mixtures with these.

*m*-Nitrobenzylidene-*p*-bromoaniline.—This was prepared by heating the appropriate aldehyde and amine together without a solvent until water vapour ceased to be given off, and crystallising the product from benzene, whence it was obtained as very pale yellow prisms, m. p. 84–85° (Found: Br = 26.2.  $C_{13}H_9O_2N_2Br$  requires Br = 26.2 per cent.).

(V) *The Reaction*  $(m) NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2 (p) + (p) NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2 (m) \rightleftharpoons \text{cycloid} \rightleftharpoons (m) NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2 (m) + (p) NO_2 \cdot C_6H_4 \cdot CH:N \cdot CH_2 \cdot C_6H_4 \cdot NO_2 (p).$ —

(a) *Formation of p-Nitrobenzylidene-p-nitrobenzylamine and m-Nitrobenzylidene-m-nitrobenzylamine from m-Nitrobenzylidene-p-nitrobenzylamine and p-Nitrobenzylidene-m-nitrobenzylamine.*—Three grams each of *p*-nitrobenzylidene-*m*-nitrobenzylamine and *m*-nitrobenzylidene-*p*-nitrobenzylamine were dissolved in 10 c.c. of ethyl acetate and the solution was kept at the ordinary temperature until crystallisation appeared to have ceased. The solid, after four crystallisations from ethyl acetate, melted at 148°, and did not depress the m. p. of pure *p*-nitrobenzylidene-*p*-nitrobenzylamine (below), with which direct comparison showed its identity. The ethyl acetate filtrate was concentrated to 5 c.c., seeded with the above dinitro-compound, filtered after half an hour, and then seeded with a crystal of *m*-nitrobenzylidene-*m*-nitrobenzylamine, which slowly separated. After two crystallisations from alcohol, the product melted at 138°, and did not depress the m. p. of pure *m*-nitrobenzylidene-*m*-nitrobenzylamine (below), with which its identity was established by direct comparison.

(b) *Formation of p-Nitrobenzylidene-m-nitrobenzylamine and m-Nitrobenzylidene-p-nitrobenzylamine from m-Nitrobenzylidene-m-nitrobenzylamine and p-Nitrobenzylidene-p-nitrobenzylamine.*—Equal quantities of *p*-nitrobenzylidene-*p*-nitrobenzylamine and *m*-nitrobenzylidene-*m*-nitrobenzylamine (below) were dissolved in the minimal quantity of boiling ethyl acetate and the solution was

kept at 60° for one hour and then cooled. No crystals separated until a trace of finely powdered *p*-nitrobenzylidene-*m*-nitrobenzylamine was added, with consequent deposition of this substance. As crystallisation proceeded, *p*-nitrobenzylidene-*p*-nitrobenzylamine and *m*-nitrobenzylidene-*m*-nitrobenzylamine began to be deposited. The ultimate residue almost certainly contained a large proportion of *m*-nitrobenzylidene-*p*-nitrobenzylamine, but it could not be entirely freed from the accompanying trace of the less soluble isomerides. The *p*-nitrobenzylidene-*m*-nitrobenzylamine was identified by its m. p. and by that of its mixture with an authentic specimen.

*p*-Nitrobenzylidene-*p*-nitrobenzylamine.—The appropriate aldehyde and base were mixed together in ethereal solution, the solvent was evaporated, and the residue recrystallised from boiling benzene. It separated in colourless needles, m. p. 150° (Found: C = 58.5; H = 4.4.  $C_{14}H_{11}O_4N_3$  requires C = 58.9; H = 3.9 per cent.), and was rather sparingly soluble in alcohol, benzene, or ether, but easily soluble in ethyl acetate or chloroform.

*m*-Nitrobenzylidene-*m*-nitrobenzylamine.—This base was prepared like the preceding one. The product separated from alcohol or benzene in glistening leaflets, m. p. 141° (Found: C = 59.0; H = 4.2.  $C_{14}H_{11}O_4N_3$  requires C = 58.9; H = 3.9 per cent.). It is extremely soluble in chloroform, moderately soluble in ethyl acetate, and rather sparingly soluble in cold benzene or alcohol.

(C) *Additive Reactions of Azomethines Leading to the Isolation of the Products of Division of the Cycloid.*

(VI) *The Reaction*  $(m) NO_2 \cdot C_6H_4 \cdot CH : NPh + CHPh : N \cdot C_6H_4 \cdot NO_2(o) \rightleftharpoons \text{cycloid} \rightleftharpoons (m) NO_2 \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot NO_2(o) + CHPh : NPh$ .—This change takes place to a considerable extent from left to right when the initial substances are allowed to react in benzene solution at the ordinary temperature for several weeks. *m*-Nitrobenzylidene-*o*-nitroaniline crystallises from the solution, whilst benzylideneaniline may be isolated by evaporating the solvent and extracting the residue with cold carbon disulphide (Found: N = 7.9 per cent.).

*m*-Nitrobenzylidene-*o*-nitroaniline forms bright yellow, feathery crystals, and, after crystallisation from benzene, melts at 143–145°. The substance obtained by the above method was identified by analysis (Found: C = 57.2; H = 3.7 per cent.), and by direct comparison and the melting point of its mixture with a specimen prepared by heating *m*-nitrobenzaldehyde with *o*-nitroaniline, without the addition of a solvent, until water ceased to be evolved (Found: C = 57.4; H = 3.4; N = 15.8.  $C_{13}H_9O_4N_3$  requires C = 57.6; H = 3.5; N = 15.5 per cent.).

(VII) *The Reaction* (*m*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:NPh} + \text{CHPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*m*)  $\rightleftharpoons$  cycloid  $\rightleftharpoons$  (*m*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*m*) +  $\text{CHPh:NPh}$ .—This change goes practically completely from left to right in the course of forty-eight hours at the ordinary temperature in benzene solution. The separation of the products was effected as in the preceding instance, and each was identified by comparison and by the m. p. of its mixture with a genuine specimen.

The *m*-nitrobenzylidene-*m*-nitroaniline, prepared either in the above manner, or by condensation of the appropriate aldehyde and base, crystallised from benzene in aggregates of pale buff-coloured needles, m. p.  $158^\circ$  (Found: C = 57.6; H = 3.5. Calc., C = 57.6; H = 3.3 per cent.). Hantzsch gives  $153^\circ$  as the m. p. (*Ber.*, 1890, 23, 2775).

(VIII) *The Reaction* (*m*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:NPh} + \text{CHPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*p*)  $\rightleftharpoons$  cycloid  $\rightleftharpoons$  (*m*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*p*) +  $\text{CHPh:NPh}$ .—This reaction requires about one month for its completion, but is otherwise very similar to reaction (VI). The products were separated and identified in the same way. Indications of the formation of the cycloid were obtained, but it could not be isolated in a pure condition.

*m*-Nitrobenzylidene-*p*-nitroaniline was prepared for comparison with the substance obtained in the above reaction by heating the appropriate aldehyde and base together without a solvent until water ceased to be evolved. The product crystallised from benzene in aggregates of olive-yellow needles, m. p.  $145\text{--}146^\circ$  (Found: C = 57.9; H = 3.6; N = 15.7.  $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_3$  requires C = 57.6; H = 3.3; N = 15.5 per cent.).

(IX) *The Reaction* (*p*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:NPh} + \text{CHPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*m*)  $\rightleftharpoons$  cycloid  $\rightleftharpoons$  (*p*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*m*) +  $\text{CHPh:NPh}$ .—This reaction is very similar to (VII) and was carried out in the same way.

*p*-Nitrobenzylidene-*m*-nitroaniline was prepared from the aldehyde and base for purposes of comparison. It separated in stout, orange prisms, m. p.  $154\text{--}155^\circ$  (Found: C = 57.8; H = 3.4. Calc., C = 57.6; H = 3.3 per cent.). Lowy and King record m. p.  $152^\circ$  (*J. Amer. Chem. Soc.*, 1921, 43, 627).

(X) *The Reaction* (*p*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:NPh} + \text{CHPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*p*)  $\rightleftharpoons$  cycloid  $\rightleftharpoons$  (*p*)  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (*p*) +  $\text{CHPh:NPh}$ .—This reaction is in all respects similar to (VIII), and was carried out in the same way.

*p*-Nitrobenzylidene-*p*-nitroaniline was prepared, for comparison, from the aldehyde and base, and obtained as bright yellow prisms, m. p.  $199\text{--}200^\circ$  (Found: C = 57.7; H = 3.6. Calc., C = 57.6; H = 3.3 per cent.). Lowy and King give m. p.  $198.5^\circ$  (*loc. cit.*).

(XI) *The Reaction*  $(p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh} + \text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} (p) \rightleftharpoons \text{cycloid} \rightleftharpoons (p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br} (p) + \text{CHPh}\cdot\text{NPh}$ .—This change takes place from left to right in the course of a few hours in benzene solution at the ordinary temperature, and in a few minutes on boiling. In the latter case the bromonitro-base crystallises on cooling (Found : Br = 26.5. Calc., Br = 26.2 per cent.).

*p*-Nitrobenzylidene-*p*-bromoaniline was also prepared, for comparison, from the appropriate aldehyde and base. It separated from benzene in short, yellow needles, m. p. 160–161° (Found : Br = 26.4 per cent.). Lowy and King record m. p. 160.5° (*loc. cit.*).

(XII) *The Reaction*  $(p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph} + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (p) \rightleftharpoons \text{cycloid} \rightleftharpoons (p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (p) + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$ .—This reaction occurs almost instantaneously when the mononitro-bases are melted together at 70–100°, and is quantitative from left to right if they are mixed in dry ether or benzene. The *p*-nitrobenzylidene-*p*-nitrobenzylamine, most of which crystallised from the solvent used, was purified by recrystallisation from alcohol, and identified by its melting point (150°) and nitrogen content (Found : N = 14.4. Calc., N = 14.7 per cent.), and by direct comparison with a known specimen. After the dinitro-compound had been caused to crystallise as completely as possible by rubbing with solvents, the oily residue was distilled under diminished pressure. After two distillations, the benzylidenebenzylamine was obtained as a pale yellow oil, b. p. 192°/30 mm. (Found : N = 7.7. Calc., N = 7.2 per cent.). It was definitely identified by hydrolysis by dilute hydrochloric acid to benzaldehyde and benzylamine, which were separated and identified by conversion into crystalline derivatives (benzaldehydesemicarbazone and benzoylbenzylamine).

(XIII) *The Reaction*  $(m) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph} + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (m) \rightleftharpoons \text{cycloid} \rightleftharpoons (m) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (m) + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$ .—This reaction was carried out like the preceding one and the products were identified in the same way. The *m*-nitrobenzylidene-*m*-nitrobenzylamine was separated by taking advantage of its insolubility in cold benzene.

(XIV) *The Reaction*  $(p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\text{Ph} + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (m) \rightleftharpoons \text{cycloid} \rightleftharpoons (p) \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 (m) + \text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$ .—This reaction was carried out by fusing the mononitro-bases together at 60°. The products were separated and identified as previously described (for the dinitro-compound : Found : N = 14.7. Calc., N = 14.7 per cent.).

(XV) *The Reaction*  $(m) \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{CH}_2\text{Ph} + \text{CHPh} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 (p) \rightleftharpoons \text{cycloid} \rightleftharpoons (m) \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 (p) + \text{CHPh} \cdot \text{N} \cdot \text{CH}_2\text{Ph}$ .—This reaction was carried out like the preceding one, and the products were identified in the same way (for the dinitro-compound: Found: N = 14.7. Calc., N = 14.7 per cent.).

(D) *Reactions Leading to the Isolation of the Factors.*

Under this head are included attempts to detect reversibility of the reactions of section C. It is unnecessary to describe these experiments, as the method is the same as in section C, and the general result has been referred to in the introduction.

(XVI) *p-Nitrobenzylidene-p-nitroaniline and excess of benzylideneaniline at 100°.*

(XVII) *p-Nitrobenzylidene-p-bromoaniline and excess of benzylideneaniline at 100°.*

(XVIII) *p-Nitrobenzylidene-p-nitrobenzylamine and excess of benzylidenebenzylamine at the ordinary temperature and at 100°.*

NOTE.—*Preparation of Benzylidene-o-nitroaniline.* This substance, which was required for experiments (III) and (VI) and had not been previously described, was prepared by heating benzaldehyde with one equivalent of *o*-nitroaniline without a solvent until the evolution of water vapour had nearly ceased. Condensation was not quantitative, but the product set to a thick paste of crystals which was purified by draining on porous porcelain and crystallising from benzene. The substance forms small, bright orange needles, m. p. 118° (Found: C = 69.2; H = 4.6.  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$  requires C = 69.0; H = 4.4 per cent.).

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### CCXXXV.—*The Composition of Paraffin Wax.* *Part III.*

By FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON.

IN the last communication (this vol., p. 1529), we described the isolation and properties of seven constant-boiling fractions obtained from paraffin wax, and pointed out that these—lettered B to H—constitute about 80 per cent. of that material.

The present account deals with the air oxidation of these and other fractions at 100°, and with the separation of the constituents of the resulting products.

We have still to prove that the constant-boiling fractions are pure or fairly pure hydrocarbons, although we believe that the argument advanced in this communication is very strong evidence in support of the view that they are not mixtures.

#### I.—*Velocity of Oxidation.*

The method employed in the oxidation of the fractions is similar to that previously described (*loc. cit.*, p. 496); it was carried out by means of a current of dry and carbon dioxide-free air at 100°.

In all cases carbon dioxide and formic acid were produced, and an estimation of these made in six cases led us to the conclusion that the amounts of carbon in both these substances correspond closely in each case with the oxidation of one gram-atom of carbon per one gram-molecule of hydrocarbon.

At suitable intervals during the oxidation, specimens were taken and analysed; their melting points and the percentage of oxygen deduced are given in Table I.

Table I gives the data for nine fractions; of these A, which is almost certainly a mixture, boils over a range of at least 10°; and residue 18—21, known to be a mixture, over a range of 30°.

Six fractions, lettered B, C, E, F, G, and Residue, were treated with 2 per cent. of turpentine, whereas A, D, and H were oxidised in the absence of this substance. The results obtained, however, and others to be communicated later, indicate clearly that oxidation would have taken place without turpentine, and that the "latent period" (*loc. cit.*, pp. 499, 1534) has been very considerably diminished by the long period of heating involved in the fractionation of the wax.

Full details of the fractions oxidised will be found in the previous communication (*loc. cit.*, p. 1532).

It will be seen that the first and the last fractions oxidise at a much slower rate than any of the others, but that whereas fraction A finally showed an oxygen content of 12.9 per cent., the amount of this element in the "residue" does not increase beyond 6.3 per cent.

Fraction G has a molecular weight of 450, and is oxidised in a manner comparable with the others, yet synthetic dotriacontane with the same molecular weight has been shown to resist oxidation under similar conditions; consequently it is perfectly clear that these two hydrocarbons are not identical.





## II.—Separation of Products of Oxidation.

The materials resulting from the oxidation of the various fractions given in Table I (the molecular weight and acid value of which are given in Table II) were dissolved in absolute alcohol, treated with an excess of a cold concentrated solution of potassium hydroxide, and made up to equal volumes of water and alcohol. The resulting solution was then repeatedly extracted with light petroleum, which removes inert material. The acids were liberated from their salts and divided into those soluble and insoluble in light petroleum. The former correspond to those previously designated as  $\alpha$ - and  $\beta$ -, and the latter to the  $\gamma$ -acids (*loc. cit.*, p. 507). The process has to be repeated in order to effect a complete separation of the inert and acidic constituents. The amounts of these two acids, expressed as a percentage of the oxidation product, together with their acid values, are given in Table II.

After the above separation had been effected, a determination of the saponification value of the various inert specimens showed the presence of esters and possibly of anhydrides; the following values were obtained for fractions A to "Residue," namely, 37.5, 39.6, 21.6, 40.2, 25.1, 54.7, 41.8, 38.8, 23.1, respectively. The inert material was consequently saponified and the acids and neutral material were separated as described above. The acids obtained from each fraction by this treatment, together with their melting points and acid values, are given in Table II and expressed as percentages of oxidation product.

The resulting neutral materials still contained unchanged hydrocarbons, which were separated by crystallisation from acetone, in which they are very insoluble in the cold. On repeating the operation several times, hydrocarbons were obtained, the analyses of which showed they were completely free from oxygen-containing substances. The neutral material, which certainly contains alcohols and very probably other oxygen derivatives, together with the unoxidised hydrocarbons, are given in Table II as percentages of oxidised product. A discussion on the latter substances is given in the next section.

In the accounts of the various separations outlined in this section, it will be realised that, to begin with, only relatively small quantities of the constant-boiling fractions of paraffin wax were available (see Table I), and, further, that repeated operations had to be carried out with the oxidised materials in order to obtain the pure constituents; in such circumstances losses were unavoidable, and their extent can be judged from the data given in Table II; it will be seen that in three cases the total loss was about 10 per cent. and in five others less than 5 per cent.

TABLE II.

Fraction.	Mol. wt.	M. p.	Oxidised product.		Free acids.				Acids as esters or anhydrides.				Alcohols, etc.		Unoxidised hydrocarbons.			
			Mol. wt.	Acid value.	M. p.	Acid value.	o/g.	Acid value.	o/g.	M. p.	Acid value.	o/g.	etc.	Mol. wt.	M. p.	o/g.	Mol. wt.	M. p.
A	291	37.8°	282	75.7	32.7	25.5°	224.9	8.8	283.0	5.0	31.2°	198.5	36.1	6.5	—	41.5°	33°	33°
B	325	44.9	321	112.8	31.9	30.4	212.5	17.8	252.0	6.1	31.8	191.2	25.3	7.7	332	45.2	45.2	45.2
C	332	51.9	328	110.9	38.1	34.8	206.3	16.4	259.3	4.3	39.5	189.2	26.0	12.8	336	51.0	51.2	51.2
D	358	53.2	332	104.5	41.7	39.5	177.2	19.2	289.2	5.7	39.4	150.5	19.6	10.7	364	53.4	53.3	53.3
E	394	57.3	414	97.3	43.1	42.3	192.3	14.3	245.2	6.1	41.5	119.3	18.5	15.0	395	56.8	57.0	57.0
F	419	60.9	419	94.2	48.5	44	146.9	10.7	240.0	8.4	44.3	168.8	12.2	17.3	414	61	61	61
G	449	63.3	450	84.3	42.8	50.2	159.7	12.5	204.6	8.4	48.4	125.4	15.0	16.7	451	63.4	63.4	63.4
H	434	66.6	436	79.9	40.3	53.5	146.7	14.3	214.1	7.0	54.4	114.0	12.3	19.2	428	66.4	66.4	66.4
Residue	528	69—72	558	29.9	28.1	62.5	86.8	2.7	—	8.5	59.5	116.6	30.4	10.1	—	—	—	—

On the other hand, mixtures of the various oxidation products can be obtained readily and in quantity from the oxidation of paraffin wax itself, and the work on which we have been engaged for some time makes it appear highly probable that a separation of such mixtures can be effected; it will then be possible to compare the resulting substances with those isolated from the oxidation of the constituent fractions of the wax, which are described in this communication.

At this stage of the investigation, it is only possible to state generally that, omitting fraction A and the Residue, the various percentages of the constituents indicate that a very similar change has been effected in all cases.

We experienced difficulties in separating the constituents of the oxidised product from the residues, fractions 18 to 21, and the data for alcohols, etc., and unoxidised hydrocarbons in this case are much less accurate than in the others.

### III.—*Nature of Unoxidised Hydrocarbons.*

The molecular weight of the hydrocarbons recovered from the oxidation mixture, together with their melting points, are given in Table II; and on comparison with the corresponding data for the fractions in columns 2 and 3 it will be seen that, within experimental error, they are the same.

It was found that determinations of the melting points of mixtures of some of the original fractions always showed a depression below that of the lower-fusing hydrocarbon; thus a mixture of equal quantities of E, m. p.  $57.3^{\circ}$ , and F, m. p.  $60.9^{\circ}$ , melts at  $53.6^{\circ}$ . It will be seen in Table II that the melting points of mixtures of fractions B to E and G with the respective hydrocarbons which escaped oxidation gave no indication that the residues were other than identical with the original fraction.

The percentage solubility of the residual hydrocarbons in chloroform at  $15^{\circ}$  was determined in the cases of those recovered from fractions B to F and found to be 20.4, 8.5, 5.6, 3.5, and 2.5, respectively, the numbers for the original fractions being 20.6, 8.38, 5.42, 3.48, and 2.0; again, the data, with the exception of that for F (in which only small quantities were available), are the same within experimental error.

Finally, we have confirmed the identity in the case of fractions C, E, F, and G by comparing the refractive indices of these with those of the corresponding hydrocarbons left unoxidised. This comparison was made at different temperatures between  $60^{\circ}$  and  $82^{\circ}$  and showed unmistakably the exact similarity of the two groups.

On the other hand, in the case of fraction A and the Residue,

known to be mixtures, the unoxidised hydrocarbons recovered were not identical with the original material.

There is no doubt that the seven fractions of constant boiling point leave small quantities of unoxidised hydrocarbons which in each case are identical with the fraction used. Now, had fraction B, for instance, consisted of a mixture of two hydrocarbons in some definite proportion, that is, a constant-boiling mixture, it is not likely that, in this case, unoxidised residue amounting to only 7.7 per cent. should consist of these two hydrocarbons in exactly the same proportion. But that such conditions should obtain in the case of six other fractions is so extremely improbable that we regard the identity of the original with the residual hydrocarbons as strong evidence that the fractions of constant boiling point isolated from paraffin wax are pure hydrocarbons and not mixtures.

Our thanks are due to the University Colston Society for grants towards the expenses of this work, and to the Department of Scientific and Industrial Research for assistance which has again enabled two of the authors (C.M.W. and R.W.W.) to take part in the investigation.

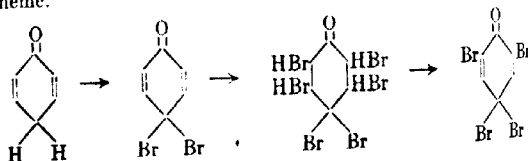
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### CCCCXXXVI.—The Mechanism of the Bromination of Phenol in Aqueous Solution.

By HARRY BAINES.

It has been shown by Dinwiddie and Kastle (*Amer. Chem. J.*, 1911, **46**, 502) that when phenol is brominated in aqueous solution only tribromophenol and tribromophenol bromide are formed, whereas on bromination in non-hydrolytic solvents such as chloroform, carbon tetrachloride, carbon disulphide, etc., substitution takes place with the formation of a dibromophenol, probably 2:4-dibromophenol. They suggest that the peculiar behaviour of phenol in aqueous solution is due to its existence in solution in the quinonoid form, the reaction taking place according to the following scheme.



In order to test this suggestion, the action of bromine on phenol in carbon tetrachloride solution was investigated. Standard solutions of phenol and of bromine in carbon tetrachloride were prepared. Known volumes of each solution were mixed, and after standing, an aqueous solution of potassium iodide was added, and the whole quickly shaken. The liberated iodine was then estimated by titration with standard sodium thiosulphate solution.

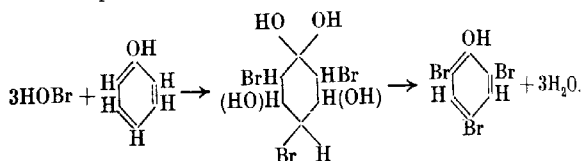
It was thus found that although phenol be left with excess of bromine in carbon tetrachloride solution during several hours, much less bromine reacts than is necessary to form the tribromoderivative. If to such a mixture water be added, the colour of the bromine becomes less intense; tribromophenol is immediately formed in the aqueous layer, and redissolves in the carbon tetrachloride.

A known volume of the phenol solution was mixed with a known excess of the bromine solution, and at certain definite intervals aliquot portions of the mixture were removed and titrated. On plotting the time against the amount of bromine reacted, a continuous curve was obtained, many days, however, elapsing before the tribromophenol stage was reached. Hence the statement of Dinwiddie and Kastle (*loc. cit.*) concerning the formation of dibromophenol expressed only a part of the truth. The velocity of the reaction also varied regularly with the concentrations of the reacting substances.

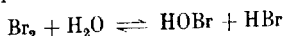
To phenol (20 grams) in carbon tetrachloride (200 c.c.), the requisite quantity of bromine solution to form monobromophenol was slowly added (34.1 grams of bromine in 200 c.c. of carbon tetrachloride) in order to test whether the product would consist mainly of a mixture of phenol and tribromophenol, or of monobromophenol. After a few minutes, when the colour of the bromine had almost disappeared, the carbon tetrachloride was evaporated, and a theoretical yield of a mixture of *o*- and *p*-monobromophenol was obtained. On similar treatment with twice the quantity of bromine, a theoretical yield of 2:4-dibromophenol was obtained, the reaction in this case taking many hours to complete. The above compounds were also prepared by treating phenol solution with excess of the bromine solution, and adding an aqueous solution of potassium iodide at the necessary time, calculated on the results of previous titrations. This method, however, proved to be less satisfactory than the former.

The degree of moisture of the solutions was also found to have an effect on the velocity of the reaction. When the moist solutions were dried with calcium chloride, the reaction was found to be retarded, and on further dehydration with zinc chloride or phosphoric oxide, the bromination was retarded still more.

From these observations and experiments, theoretical conclusions can be drawn bearing on the mechanism of the bromination of phenol. If the reaction takes place by direct substitution, there is no reason why bromination should not be effected as readily in non-hydrolytic solvents as in water. Also the accelerating effect of a trace of water is inexplicable on this theory. The different characters of the reactions in water and carbon tetrachloride are illustrated by the difference in velocity and in products of incomplete bromination. However, these facts and several others are explained on the assumption that the slow reaction between dry phenol and dry bromine in an inert solvent is one of direct substitution, whereas the rapid bromination of phenol in aqueous solution is due to the action of hypobromous acid, formed by the interaction of bromine and water. The hypobromous acid probably reacts with the phenol by addition, with subsequent elimination of water.



The removal of the hypobromous acid from the system during bromination in aqueous solution causes the reaction



to proceed to completion from left to right, hydrobromic acid being formed as a by-product. The water in the reaction cycle is constant in amount and therefore acts as a pseudo-catalyst. This explains the accelerative action of a trace of water in the bromination in carbon tetrachloride solution.

In order to test the above suggestion, the action of hypobromous acid on phenol was investigated. A very dilute solution of hypobromous acid was made from bromine water and zinc oxide. On treatment with a little phenol a slight white precipitate was obtained, and potassium iodide-starch paper proved that the hypobromous acid had reacted. A large volume of the suspension having been extracted with a little carbon tetrachloride, the precipitate was proved to be tribromophenol.

The behaviour of hypobromous acid towards phenol is evidence in favour of the mechanism suggested, which is further supported by the fact that bromination is retarded by conditions hindering the formation of hypobromous acid from bromine and water. One such condition would be bromination in the presence of a large

excess of hydrobromic acid, or indeed in any strongly acid solution. Pope and Wood (T., 1912, 101, 1823) describe the bromination of phenol in concentrated hydrobromic acid solution, and state that the bromine is absorbed very slowly by the phenol. They recommend this method for the preparation of dibromophenol. Dinwiddie and Kastle (*loc. cit.*) mention the retarding effect of glacial acetic acid, and Hewitt, Kenner, and Silk (T., 1904, 85, 1225) show that concentrated sulphuric acid mixed with the glacial acetic acid retards the bromination still more.

The author desires to express his indebtedness to Professor F. S. Kipping, F.R.S., for his interest in this work, and to the Department of Scientific and Industrial Research for a grant which has enabled him to carry out this investigation.

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### CCXXXVII.—*The Equilibrium in Systems Composed of Water and Alcohols: Methyl Alcohol, Pinacene, Glycerol, and Erythritol.*

By NICOLAI ANTONOVICH PUSHIN AND ALEXANDRA  
ALEXANDROVNA GLAGOLEVA.

#### *The System Methyl Alcohol-Water.*

In a previous communication (*J. Russ. Phys. Chem. Soc.*, 1915, 47, 100) it was shown that, contrary to statements in the literature, ethyl alcohol does not form a definite hydrate with water. With methyl alcohol also, the existence of a long series of definite compounds with water has been inferred from various properties of the solutions (Varenne and Godefroy, *Comp. rend.*, 1904, 138, 990; De Forcrand, *Ann. Chim. Phys.*, 1892, [vi], 27, 546; Jones and Getman, *J. Amer. Chem. Soc.*, 1910, 32, 308). As will be shown in this communication, the study of the equilibrium in the system methyl alcohol-water does not support the supposition that there exists any definite chemical compound of the two substances.

The freezing points of mixtures of methyl alcohol and water were determined by Pickering (T., 1893, 63, 1015) up to 50 mols. per cent. of alcohol, and by Baume and Borovsky over the whole range (*J. Chim. physique*, 1914, 12, 276), but neither of these authors examined the eutectic freezing points, so that no conclusions can be drawn from their work as to the existence of solid compounds.

Many temperatures recorded by Baume and Borovsky are far



too low, owing to supercooling, some of them lying considerably below the true eutectic temperature.

The investigation of the equilibrium in the system methyl alcohol-water was carried out according to the method employed in the case of the system ethyl alcohol-water (*loc. cit.*). The mixture to be examined was placed in a glass vessel, which was enclosed in two or three glass mantles, and the whole system was cooled with liquid air. The temperature was recorded by a thermo-element and a galvanometer.

If the necessary precautions are not taken, methyl alcohol and many of its mixtures with water, when cooled to the temperature of crystallisation, do not crystallise at all but become transformed into a hard, glassy mass. In order to induce crystallisation it is necessary that at temperatures near the point of crystallisation the rate of cooling be very slow and that the mixture be continually stirred.

The results of the study of the system methyl alcohol-water are given in Table I and Fig. 1, A.

TABLE I.  
Methyl alcohol and water.

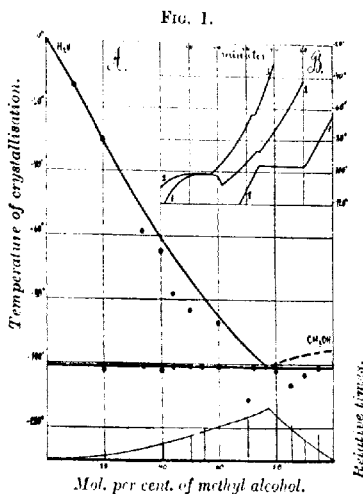
Concen- tration of methyl alcohol in mol. %	Temperature of first crystal- lisation.	Temperature of eutectic crystal- lisation.	Duration of eutectic crystallis- ation in minutes for 1 gram of substance.	Concen- tration of methyl alcohol in mol. %	Temperature of first crystal- lisation.	Temperature of eutectic crystal- lisation.	Duration of eutectic crystallis- ation in minutes for 1 gram of substance.
0		0°		60	-87.5°	-101.5°	
10	-13.5°			70		-111	1.2
20	-30.2	-102°	0.1	72		-101	
33.3	-59	-100.5		80		-102	1.3
40	-65	-102	0.4	85		-107	1.1
44	-78.5	-100.5		90		-103.5	0.6
50	-83.5	-100.5	0.7	95		-100.5	0.8
54		-100.5	1.0	100		-96°	

Pure methyl alcohol crystallises at -96°. Its cooling curve, which is that characteristic of a pure substance, is shown in Fig. 1, B, 1-1.

Solutions with a content of 10-60 mol. per cent of alcohol gave a definite temperature of first crystallisation (in most cases with great overcooling), and also a definite temperature of eutectic crystallisation. Fig. 1, B, 2-2 and 3-3 show the cooling curves for solutions containing 60 and 40 mol. per cent. of alcohol, respectively.

In solutions with a content of more than 60 mol. per cent. of

alcohol the temperature of first crystallisation could not be determined. For this reason the branch of the diagram connecting the freezing point of pure alcohol and the eutectic point remained undetermined. The eutectic crystallisation at  $-100.5^{\circ}$  was determined over the whole range of composition. Some of the solutions showed a great overcooling of the eutectic point. By repeated determinations, this point was raised from  $-122^{\circ}$  to  $-103.5^{\circ}$  in the case of 90 mol. per cent. of alcohol, and from  $-110.5^{\circ}$  to  $-107^{\circ}$  in the case of 85 mol. per cent. of alcohol. For mixtures of 80 and 72 mol. per cent. of alcohol, not only the cooling curve, but also the heating curve was determined. The melting point for the first mixture was determined as  $-102^{\circ}$ , for the second as  $-101^{\circ}$ . The temperature for the second mixture is very close to that obtained by the method of cooling ( $-102^{\circ}$ ). As concerns the position of the eutectic point, the maximum of the duration of crystallisation at the eutectic temperature ( $-100.5^{\circ}$ ) was determined for a mixture containing 80 mol. per cent. of alcohol. Near this ordinate is the eutectic point.



It will be seen that the equilibrium diagram of the system methyl alcohol-water is characterised by two branches, which cross at the eutectic point and can be traced through the whole diagram. It follows, therefore, that in the crystalline state methyl alcohol does not form any definite compound with water. Both substances give mechanical mixtures only.

Since the calorific effect is positive when methyl alcohol is mixed with water (De Forcrand, *loc. cit.*), it follows that hydrates of a definite composition, if they exist at all, should be of an exothermic nature. Their stability should increase with decrease of temperature and with the transition from the liquid to the solid state. Therefore it can be stated with great probability, that if definite compounds of methyl alcohol and water do not exist in the

TABLE II.  
Pinacone and water.

Concen- tration of pinacone in mol. %.	Temperature of first of eutectic crystal- crystal- lisation.	Duration of eutectic crystallis- ation in minutes for 1 gram of substance.	Concen- tration of pinacone in mol. %.	Temperature of first of eutectic crystal- crystal- lisation.	Duration of eutectic crystallis- ation in minutes for 1 gram of substance.
0	0°		31.1	43.3	
0.5	16.7°	— 0.45°	34.3	41.8	
0.79	22.4	— 0.45	36.5		
0.86	22.0		37.8	40.7	2.0
1.3	23.0		39.6	40.6	1.9
2.0	33.8		40.0		
2.2	34.7	— 0.5	42.0	39.6	1.4
2.7	37.4		45.0	41.2	
3.6	40.2	— 0.5	50.0	41.25	
5.1	42.6	— 0.6	53.3	41.2	
5.5	43.2	— 0.4	57.5	41.0	27.2
6.5	43.7	— 0.6	63.7	39.4	28.2
8.0	44.4	— 0.7	64.8	39.5	27.6
9.6	44.9	— 0.7	70.8	36.6	29.2
11.6	45.2	— 1.0	75.0		29.3
12.7	45.3	— 1.5	76.4	33.7	29.3
14.27	45.4	—	80.4		29.4
14.34	45.4	—	82.8	30.2	
17.0	45.3		86.2	32.4	29.1
19.5	45.2	37.3	87.0	33.2	29.35
21.9	45.1	37.8	93.4	38.6	
24.4	44.6	40.1	97	39.7	
29.1	43.7	40.2	100	41.1°	

crystalline state below  $-100^{\circ}$ , their existence in the liquid state at the ordinary temperature is still less probable.

#### The System Pinacone-Water.

Fittig (*Annalen*, 1859, **110**, 25; 1860, **114**, 54) showed the existence of a hydrate of pinacone with the definite composition  $C_6H_{14}O_2 \cdot 6H_2O$ . Linnemann (*Annalen Suppl.*, 1864, **3**, 374; *J. Chem. Soc.*, 1871, **24**, 422) found that pure pinacone melts at  $35-38^{\circ}$  and its hydrate at  $46.5^{\circ}$ . Couturier (*Ann. Chim. Phys.*, 1892, [vi], **26**, 479) states that the melting point of pinacone hydrate is  $56^{\circ}$ . Systematic investigation of the system pinacone-water has not hitherto been carried out.

The cooling curve of commercial pinacone was of the kind characteristic of an impure substance (the first crystals were deposited at  $33^{\circ}$  and the eutectic temperature appeared to be  $29.4^{\circ}$ ; Fig. 2, B, 1—1). It was necessary, therefore, to purify the substance before investigation. After several crystallisations, the freezing point rose from  $33^{\circ}$  to  $41.1^{\circ}$ , and the eutectic point at  $29.4^{\circ}$  disap-

peared completely (Fig. 2, B, 2—2). Further purification did not change the temperature of crystallisation.

Contrary to the behaviour of methyl and ethyl alcohols, pinacone and its aqueous solutions crystallise well. A slight overcooling can easily be avoided by stirring the liquid and by inoculation with crystals. On account of the great volatility of pinacone, superfluous heating of its solution should be avoided in order to prevent perceptible change in concentration.

The results of the investigation are given in Table II and shown graphically in Fig. 2, A.

The equilibrium diagram consists of five branches:

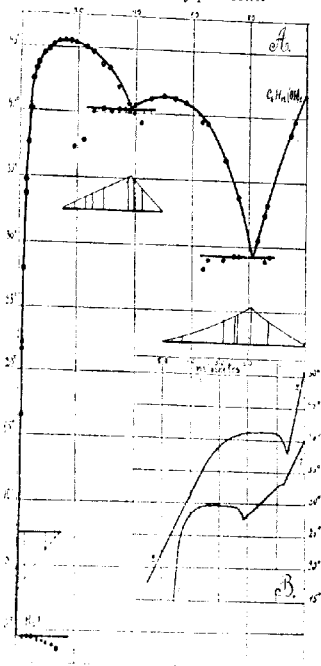
1. From pure pinacone to a mixture containing 80 mol. per cent. of pinacone. To the latter composition corresponds a eutectic point at  $29.4^{\circ}$ . The duration of the eutectic crystallisation renders improbable the existence of solid solutions of water in pinacone.

2. From 80 mol. per cent. to 50 mol. per cent. of pinacone. The eutectic crystallisation in this section is very prominent and can be traced up to the maximum of the curve. This maximum corresponds to a definite compound of pinacone and water, the monohydrate,  $C_6H_{12}(OH)_2 \cdot H_2O$ . It crystallises at  $41.25^{\circ}$ . The curve is very flat on both sides of this maximum.

3. From 50 mol. per cent. to 38.5 mol. per cent. of pinacone. To the latter composition corresponds a second eutectic point at  $40.4^{\circ}$ .

4. From 38.5 to 14.3 mol. per cent. of pinacone. The curve rises again and reaches, at 14.3 mol. per cent., a maximum, which corresponds to another compound of pinacone and water, the hexahydrate,  $C_6H_{12}(OH)_2 \cdot 6H_2O$ , which crystallises at  $45.4^{\circ}$ . This compound was described for the first time by Fittig. The statement

FIG. 2.  
Mol. per cent. of pinacone.



of Couturier that it crystallises at  $56^{\circ}$  is incorrect. The eutectic crystallisation at  $43^{\circ}$  can be traced through the whole section from 38.5 to 14.3 mol. per cent. of pinacone.

5. From 14.3 mol. per cent. of pinacone to pure water. The phenomenon of overcooling at the eutectic temperature becomes more marked with increasing content of pinacone (from  $-0.45^{\circ}$  to  $-1.5^{\circ}$ ). The eutectic temperature can be traced up to the hexahydrate.

Investigation of the system pinacone-water established the existence of two definite compounds, the monohydrate,  $C_6H_{12}(OH)_2 \cdot H_2O$  (m. p.  $41.25^{\circ}$ ), and the hexahydrate,  $C_6H_{12}(OH)_2 \cdot 6H_2O$  (m. p.  $45.4^{\circ}$ ); and the existence of two eutectic mixtures, containing respectively 80 mol. per cent. (m. p.  $29.4^{\circ}$ ) and 38.5 mol. per cent. (m. p.  $40.4^{\circ}$ ) of pinacone.

#### *The System Glycerol-Water.*

The sample of glycerol crystallised at  $13.3^{\circ}$  instead of  $17^{\circ}$ , the value given by Henninger (*Ber.*, 1875, 8, 643). In order to purify it, the specimen was exposed to quicklime for some time and distilled in a vacuum; it then crystallised at  $18.0^{\circ}$ . It was not found possible to raise the crystallisation point above this value. The purified material crystallised well, formed colourless crystals, and gave the characteristic cooling curve of a pure substance. As is well known, crystallisation of glycerol without inoculation is very difficult. Stirring alone is not sufficient; the cooled liquid does not crystallise, but is transformed into a gelatinous, transparent mass, as in the case of some other alcohols. Crystallisation becomes more difficult as the water content increases. From solutions the concentrations of which are near the eutectic concentration glycerol crystallises with very great difficulty. Solutions containing 70–75 mol. per cent. of glycerol could not be induced to crystallise at all.

The mixture under examination was cooled either at once by solid carbon dioxide or successively by a mixture of snow and salt and by solid carbon dioxide. In order to make the rate of cooling slower, the mixture was enclosed in two glass mantles.

The results of the investigation are given in Table III, and shown graphically in Fig. 3, A. Fig. 3, B shows the cooling curve of pure glycerol.

As has already been shown, pure glycerol crystallises at  $18.0^{\circ}$ . The addition of water lowers the temperature of crystallisation. By interpolation of the values from Table III, it can be seen that the temperature of first crystallisation at  $13.3^{\circ}$  corresponds with a concentration of water of 11.3 mol. per cent. or 2.25 per cent. by

TABLE III.  
Glycerol-water.

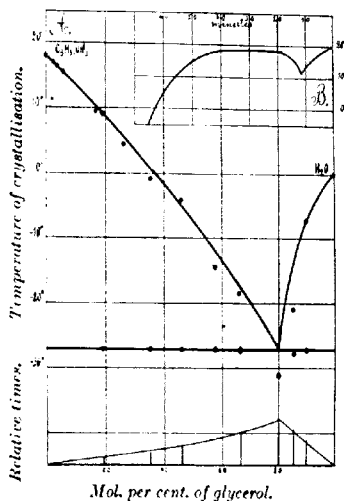
Concen- tration of water in mol. %.	Temperature of first crystal- lisation.	Duration of eutectic crystallis- ation in minutes for 1 gram of substance.	Concen- tration of water in mol. %.	Temperature of first crystal- lisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.
0	18.0°		46.0	-4.3	-27.7
1.8	17.3°		58.0	-14.7	-28.0
2.8	16.9		66.4	-18.5	-28.0
5.5	15.7		80.0	-31.0(?)	0.5
17.0	9.5		85.0	-21.0	-28.2
18.8	9.1	-27.7°	90.0	-7.5	-28.0
26.5	4.8		100	0°	
35.1	-1.3	-27.7			

weight. This was the quality of the sample of glycerol before purification.

The diagram of the system consists of two branches which cross at the eutectic point. This point corresponds to a temperature of 28.0° and an average concentration of glycerol of 20 mol. per cent. Owing to the reluctance to crystallisation of mixtures near the eutectic composition, it was very difficult to determine precisely the concentration corresponding to the eutectic point. Eutectic crystallisation was observed with all the solutions investigated. The duration of eutectic crystallisation, determined for 1 gram of the mixture, shows that water does not form a solid solution with glycerol. In the crystalline state, both substances form only a mechanical mixture.

A sample of pure glycerol being available, it seemed of interest to determine the hitherto unknown cryoscopic constant. Although the difficulty of crystallising glycerol did not allow of great precision,

FIG. 3.



yet the values obtained agreed moderately well with one another. The results are recorded in the following table.

TABLE IV.

The determination of the cryoscopic constant of glycerol.

Weight of glycerol in grams.	Weight of water in grams.	$\Delta t$ .	K for 1000 grams of solvent.
11.4474	0.0435	0.690°	3.27
10.7008	0.0610	1.116	3.52
11.4474	0.1297	2.326	3.69

The lowering of the freezing point of pure glycerol was determined with the aid of a Beckmann thermometer. Crystallisation was attained by inoculation with a small crystal of glycerol. Without the latter precaution, overcooling of the mixture could not be prevented. As shown in Table IV, the cryoscopic constant for 1000 grams of substance lies within the limits 3.27 and 3.69. As the most accurate value for the constant corresponds to the most dilute solution, we can, by extrapolating to 0, assume that the cryoscopic constant of glycerol, determined for 1000 grams of the solvent, is nearly 3.1.

From Table IV it will be seen that a mixture containing 11.4474 grams of glycerol and 0.0435 gram of water, that is, with a content of 0.38 mol. per cent. of water, has a freezing point 0.69° lower than that of pure glycerol. A depression of the freezing point of 1.82° therefore corresponds to a content of 1 per cent. by weight of water, and a depression of 0.1° corresponds to a content of 0.055 per cent. by weight of water. As depressions smaller than 0.1° can be easily detected with the Beckmann thermometer, it is obvious that the determination of the freezing point of glycerol affords a sensitive and precise method for the quantitative estimation of even small quantities of water in glycerol.

#### *The System Erythritol-Water.*

A sample of erythritol showed a crystallisation point of 116.6° instead of 120°, the temperature given by Ruff (*Ber.*, 1899, 32, 3677). As only a small quantity of the erythritol was available, the crystallisation point of the pure substance could not be determined. However, the cooling curve of the sample (Fig. 4, B) was not unlike that of a pure substance.

All our investigations were made with this sample. Both pure erythritol and its aqueous solutions crystallise moderately well, yet to avoid overcooling it was necessary to inoculate with a crystal

TABLE V.  
Erythritol-water.

Concentration of erythritol in mol. %	Temperature of first of eutectic crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.	Concentration of erythritol in mol. %	Temperature of first of eutectic crystallisation.	Duration of eutectic crystallisation in minutes for 1 gram of substance.
100	116.6°		17.5	54.6	-4.2
92.4	114.0°		14.4	40.4	
91	113.2	-11.5°	13.4	36.5	-4.4
80	110.2	-7.2	11.1	27.4	-4.4
75.2	106.5		9	22.8	-4.1
65.7	102.5		7.0	14.0	-4.4
56.4	97.5	-4.3	4.8	-1.0	-4.4
42.4	87.8	-4.4	3.0		-4.1
38.0	82.0		2.5	-3.1	-4.5
33.3	76.2	-4.1	2	-2.4	
29	70.5	-4.2	0.9	-1.1	
26.1	65.0	-4.7	0	0°	

of erythritol. The results are recorded in Table V and shown graphically in Fig. 4, A.

It will be seen that the diagram of the system erythritol-water consists of two branches, which cross at the eutectic point. The concentration of erythritol at this point is 3 mol. per cent. and the temperature  $-4.4^{\circ}$ . The eutectic crystallisation can be followed through the whole diagram. Erythritol forms with water neither compounds nor solid solutions, and in the crystalline state, erythritol and ice yield mechanical mixtures only.

The determination of the cryoscopic constant of water, with erythritol as solute, gave the value 1.94 for 1000 grams of the solvent as the mean of three determinations, which is near the theoretical value 1.86. This fact

FIG. 4.

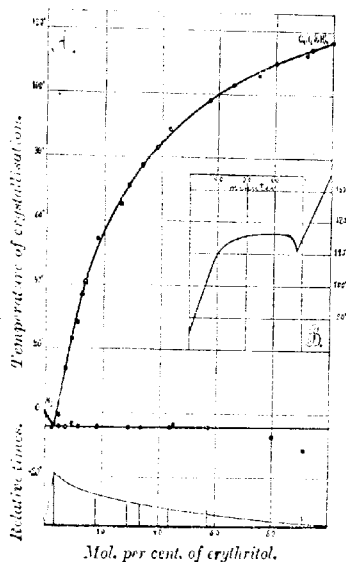




TABLE VI.

Grams of water.	Grams of erythritol.	$\Delta t$ .	The cryoscopic constant calculated for 100 grams of the solvent.
12.3414	0.5598	0.724°	19.5
12.3414	0.8648	1.097	19.1
12.1644	1.5504	2.06	19.6
			Mean 19.4

confirms our conclusion that erythritol does not form solid solutions with water.

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### CCCXXXVIII.—*The Equilibrium in the System m-Dinitrobenzene-Urethane.*

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PURE *m*-dinitrobenzene crystallises at 90°, and pure urethane at 48.3°. To determine the temperature of crystallisation of mixtures, as well as of the pure substances, the cooling curve was examined. The results are shown in the following table and in the figure. The lower curve shows the time of eutectic crystallisation.

The system *m*-dinitrobenzene-urethane.

Concentration of urethane in mol. per cent.	Temperature of		Duration of the eutectic crystallisation in minutes for 1 gram of substance.	Concentration of urethane in mol. per cent.	Temperature of		Duration of the eutectic crystallisation in minutes for 1 gram of substance.
	first crystallisation.	eutectic crystallisation.			first crystallisation.	eutectic crystallisation.	
0	90°			75	56.7°	41.6°	3.2
10	85.8°	39.5°	0.3	85	46.8	41.9	3.5
20	81.6	42.0	0.5	90	43.6	42.1	4.7
30	77.5	41.0	1.0	94	45.0		
40	73.6	42.3	1.3	96	46.0		
50	71.2	41.6	1.7	97	46.5		
66.7	64 (?)	42.3		100	48.3°		

It will be seen that with increasing content of urethane, the temperature of the first crystallisation decreases from 90° to 42.3°. To this range of temperature corresponds the eutectic crystallisation, which can be followed through the whole interval from 0 to 90 mol. per cent. of urethane. The eutectic point corresponds probably

to a concentration of 91 mol. per cent. of urethane. From the repeated detailed determinations of the cooling curve for mixtures containing 97, 96, and 94 mol. per cent., we could not infer the existence of any eutectic crystallisation in the interval from 91 to 100 mol. per cent. of urethane. The cooling curves obtained were those characteristic of the freezing of solid solutions.

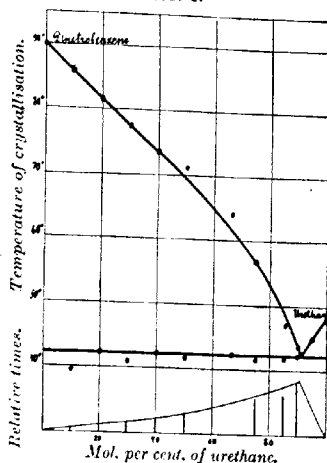
To ascertain whether solid solutions were formed, a cryoscopic determination was made with a solution of 1.34 grams of *m*-dinitrobenzene in 17.10 grams of urethane. The lowering of the crystallisation point of urethane amounted to  $2.33^\circ$ . From this the molecular constant can be calculated:  $K = 168.0 \times 2.33 \times 17.10 / 1.34 = 50.0$ .

The value calculated by van't Hoff's formula from the observed heat of fusion of urethane is 50.0. From this agreement it is evident that *m*-dinitrobenzene gives in urethane a normal lowering of the crystallisation point, and therefore, in the interval from 91 to 100 mol. per cent. of urethane, solid solutions with *m*-dinitrobenzene cannot be formed. The solid phase of the system *m*-dinitrobenzene-urethane must be, at every concentration, a mechanical mixture.

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FIG. 1.

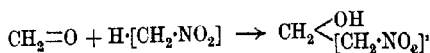


### CCXXXIX.—Formation of $\gamma$ -Alkylidene Derivatives from Ethylidenemalonic Ester.

By LUCY HIGGINBOTHAM and ARTHUR LAPWORTH.

MANY hydrogen compounds, although not themselves electrolytes, can under certain conditions take part in reactions, the gross results of which indicate that hydrogen atoms in these compounds

functionate as positively polar labile atoms. Thus nitromethane in presence of certain catalysts reacts with formaldehyde in such a way that the total result may be expressed by the equation



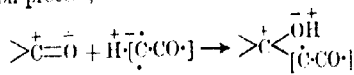
superficially a complete parallel with the reaction between hydrogen cyanide and formaldehyde,



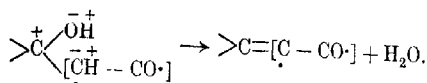
Whatever be the true mechanism of such reactions of non-acidic hydrogen compounds, it is evident that the hydrogen atom has at least a latent positive polar character, in every compound which thus simulates in its reactions the characters of an electrolyte. This was a generalisation made use of by one of us in deciding the polarities of the atoms in carbonyl compounds, and in deducing therefrom the principle of induced alternate polarities (*Mem. Manchester Phil. Soc.*, 1920, 64, ii, 3).

No doubt in many cases, perhaps in all, the equations which indicate the gross results of the change from which latent polarities of atoms have been deduced do not represent the true mechanism of the reactions. It is, for example, almost certain that the hydrogen compound is often in the first instance transformed into an isomeric or tautomeric form; but the principle of induced alternate polarities applies without taking this circumstance into consideration, and for the reason that in the reversible tautomeric transformations the atoms alter their relative position, without changing their polarities, alterations of polarity being usually associated with irreversible transformations.

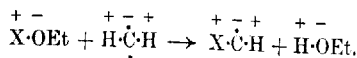
The groups  $\dot{\text{C}}\text{H} \cdot \text{NO}_2$ ,  $\dot{\text{C}}\text{H} \cdot \text{CN}$ ,  $\dot{\text{C}}\text{H} \cdot \text{CO} \cdot$  are typical of a series of arrangements containing a hydrogen atom which is non-ionisable, but which has latent positive polar character. The latent positive polar character of hydrogen directly attached to carbon is shown in a variety of reactions, and of these there may here be mentioned additive reactions with carbonyl such as that represented by the first equation in the present paper, and which corresponds with the "aldol addition process,"



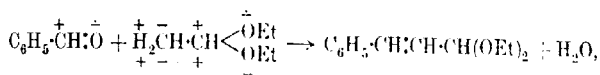
to which the "crotonic aldehyde condensation" is often the sequel:



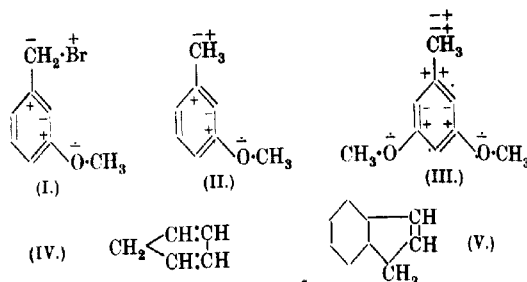
The "acetoacetic ester condensation," a term generally applied to any reactions in which a carbonyl compound containing the group  $\cdot\text{CH}_2\text{CO}\cdot$  is condensed with an ester with the aid of sodium (or potassium), its amide or its ethoxide, is a reaction typical of many compounds containing the group  $\cdot\text{CH}_2\text{CO}\cdot$ , and applies not only to  $\cdot\text{CH}_2\text{CO}\cdot$  in direct attachment to  $\cdot\text{CO}\cdot$ ,  $\cdot\text{CN}\cdot$ , etc., but also to  $\cdot\text{CH}_2\text{CO}\cdot$  in the γ-position in, for example, ethyl crotonate and in the corresponding γ- or ortho-position in *o*-nitrotoluene:



In nearly all the cases above mentioned, reactivity is associated with induced alternate polarity effects originating in oxygen or nitrogen atoms situated in certain positions elsewhere in the molecule. It is possible, however, that the true function of the polarity induced by the oxygen or nitrogen atoms is simply an auxiliary one, merely reinforcing a reactivity, already inherent in a certain configuration of the molecule but difficult to detect. Were the induced polar character of the hydrogen atom the sole origin of the "aldol addition process," the "crotonic aldehyde condensation," or the "acetoacetic ester synthesis," then compounds such as the acetals of aldehydes and ketones would be expected to undergo analogous changes; for example—

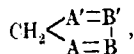


but no case of the extension of such reactions to acetals has hitherto been observed, and special attempts made by the present authors to condense ordinary acetal with benzaldehyde, ethyl oxalate, or ethyl nitrite gave entirely negative results. The authors have also attempted to condense ethyl oxalate and alkyl nitrites with *m*-tolyl methyl ether (II), and with oreinol dimethyl ether (III), but again without success, although a strong induced polar effect on the hydrogen atoms of the methyl group was to be expected; especially in the last-named case, a definite induced positive polar character having already been established for halogen in the *m*-methoxy-benzyl bromide (I) corresponding with the former (II):



Furthermore, the reactions in question have been found to take place with compounds which contain carbon and hydrogen only; pentadiene (IV) and indene (V), for example, yield benzylidene, oxalyl, and isonitroso-derivatives (*Ber.*, 1895, 28, 1501; 1900, 33, 666, 771, 3395).

For such reasons as these, the authors are inclined to the view that the capacity of esters like ethyl crotonate to condense with ethyl oxalate (and also, as will be shown in the present paper, with aldehydes) in the  $\gamma$ -position, is really conditioned by the presence of the group  $\text{CH}_2\text{--}\dot{\text{C}}=\dot{\text{C}}$  or, perhaps, more generally, of the group  $\text{CH}_2\text{A=B}$ , and to suppose that the reactivity of this group is usually insufficient unless enhanced, (1) by duplication within a ring,



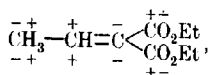
as in pentadiene and indene, or (2) by induced polarity effects, as, for instance, when B, or an atom suitably placed but still further removed, is oxygen or nitrogen.

Direct condensation of aldehydes with open-chain aliphatic carbonyl compounds at any point in the latter other than the  $\alpha$ -position with regard to the carbonyl group has been observed only in the experiments of Raper (*T.*, 1907, 49, 1627) and of Smedley (*ibid.*, 1911, 49, 1627), who obtained, from crotonic aldehyde and from aldol, compounds with normal chains of eight carbon atoms, indicating the occurrence of condensation at the  $\gamma$ -position with regard to one carbonyl group. In alicyclic compounds, two fairly clear cases are known: thus  $\Delta^4$ -*p*-menthene-3-one appears to yield an  $\alpha\gamma$ -dibenzylidene derivative (Wallach, *Annalen*, 1913, 397, 216), and piperitone a  $\gamma$ -monobenzylidene derivative (Simonsen, *T.*, 1921, 119, 1648). The formation of these products is in accordance with the principles stated above.

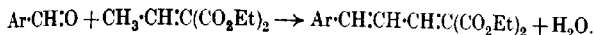
\*In the present paper are described the results of experiments made

with the object of adding to the examples of this type and of securing further evidence as to the course they follow. In the aromatic series, the nearest analogue to the reactions studied is the preparation of a benzylidene derivative from 2:4-dinitrotoluene (*Ber.*, 1904, 37, 4463).

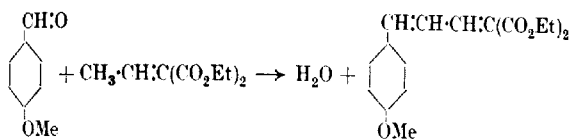
Ethyl crotonate does not yield a γ-benzylidene derivative, but ethyl ethyldenemalonate,



which differs only in having an additional carbethoxy-group attached to the same carbon atom as the first, has been found to react with aromatic aldehydes in presence of catalysts such as concentrated sulphuric acid, yielding γ-alkylidene derivatives :

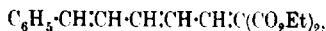


The esters, the first products, were not themselves isolated owing to practical difficulties in effecting their purification, but the corresponding acids were obtained on hydrolysis of the crude product and, in one or two cases, in yields which amounted to 50 per cent. of those theoretically possible. This was the case when benzaldehyde was used and also with anisaldehyde, from which the new acid, *p-methoxycinnamylidenemalonic acid* was obtained, indicating that the following reaction had taken place :



Piperonal offered greater practical difficulties and the yields of condensation product were smaller, but piperonylmalonic acid and from it piperic acid were successively obtained and identified.

The product to be expected by the condensation of the ester with cinnamaldehyde would be of very considerable interest because of the long series of conjugate linkages which it would contain,



but, so far, this or the corresponding acid has not been isolated.

#### EXPERIMENTAL.

*Ethyl Ethyldenemalonate and Benzaldehyde.*—These compounds were mixed in the proportion of 5.5 grams of the former and 3 grams

of the latter, six drops of concentrated sulphuric acid were added, and the whole was shaken. The mixture at once turned brown and a slight rise in temperature took place. To complete the reaction, the mixture was heated for one hour on the steam-bath, and the product was finally subjected to treatment with a current of steam to remove excess of benzaldehyde, boiled with excess of dilute aqueous sodium hydroxide for about an hour, and the resulting solution filtered from a little tarry matter. On addition of dilute sulphuric acid to the filtrate, a pale brown solid was formed, the quantity corresponding with a 50 per cent. yield of cinnamylidenemalonic acid; it crystallised from boiling alcohol in needles, melting and decomposing at  $212^{\circ}$  (Liebermann, *Ber.*, 1895, 28, 1439, gave the melting point as  $208^{\circ}$ ) (Found: C = 65.6; H = 5.1. Calc., C = 66.1; H = 4.5 per cent.). The equivalent, determined by titration against  $N/10$ -sodium hydroxide, was 109.5; a dibasic acid of the above formula requires 109.0.

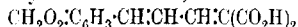
*Ethyl Ethylidenemalonate and Anisaldehyde. Formation of p-Methoxycinnamylidenemalonic Acid*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})_2$ .—These compounds, in the proportion of 1.36 grams and 1.86 grams, respectively, were mixed and shaken with four drops of concentrated sulphuric acid. The whole was warmed on the water-bath as before, purified in a current of steam, and hydrolysed by dilute aqueous sodium hydroxide, the solution cooled, filtered, and acidified. An orange-coloured precipitate of *p-methoxycinnamylidenemalonic acid* was obtained, in quantity amounting to about 55 per cent. of that theoretically possible (Found: C = 60.1; H = 5.1.  $\text{C}_{13}\text{H}_{12}\text{O}_5$  requires C = 60.4; H = 4.7 per cent.). The equivalent found was 125, that required for a dibasic acid,  $\text{C}_{13}\text{H}_{12}\text{O}_5$ , being 124.

The acid dissolves readily in alcohol, acetone, glacial acetic acid, or ethyl acetate, less readily in chloroform, and is sparingly soluble in light petroleum. It crystallises from ethyl acetate in orange-coloured needles, melting and decomposing if heated slowly at  $189^{\circ}$ ; but if the containing capillary tube be plunged into a bath, the acid does not melt at once unless the temperature of the liquid in the bath is  $203^{\circ}$ , and this may therefore be assumed to be the correct melting point. A solution of the acid in dilute sodium carbonate discharges the colour of potassium permanganate very rapidly, and the odour of anisaldehyde becomes perceptible. When the acid is heated in a vacuum, it loses carbon dioxide and a pale yellow solid distils; this is no doubt *p-methoxycinnamylidenemalonic acid*, but was not closely characterised.

*Ethyl Ethylidenemalonate and Piperonal.*

(With CHARLES SIMPSON.)

When equimolecular proportions of ethyl ethylidenemalonate and piperonal are mixed and warmed with sulphuric acid (about one drop for each 0.8 gram of the mixture) at 60° for three hours, and the product then treated as in the experiments already described, a mixture of acids is obtained, which, calculated as piperonylenemalonic acid, represents about 37 per cent. of the calculated quantity. This, however, is not a uniform substance, and after being purified by solution in aqueous sodium carbonate, reprecipitation with dilute sulphuric acid, careful washing and drying, gave the following analytical results: C = 65.0, 64.5; H = 3.7, 3.8. The equivalent, determined by titration against *N*/10-alkali, was 187. These results correspond fairly well with the assumption that the material is a mixture of piperonylenemalonic acid,



(Calc., C = 59.5; H = 3.8 per cent.; equivalent = 131), and piperic acid,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$  (Calc., C = 66.1; H = 4.6 per cent.; equivalent = 218) in the proportions 3:7. There can be little doubt that this roughly represents the character of the acid product, as when it is boiled with a large quantity of hot water, the filtered solution on cooling deposits a bright red powder which melts at 200–204°, and is fairly pure piperonylenemalonic acid. Scholtz (*Ber.*, 1895, 28, 1189) describes this acid as crystalline, separating from alcohol as a brick-red mass of small needles melting at 205–206°. As a complete separation of the two constituents was not found practicable, the mixture was boiled with a large excess of acetic anhydride, which, according to Scholtz, converts the dicarboxylic acid into piperic acid; in this manner, the mixture yielded rather more than one-half its weight of piperic acid (Found: C = 65.4; H = 4.6 per cent.). The piperic acid separated from hot water, in which it was sparingly soluble, as a yellow, micro-crystalline powder melting at 210°.

*Ethyl Ethylidenemalonate and other Aromatic Aldehydes.*—Experiments were made on the condensation of the ester with salicylaldehyde and cinnamaldehyde and there was evidence that condensation takes place in both instances, but the nature of the crystalline products obtained has not yet been decided; their investigation will be continued.

*Experiments on Acetal, on m-Tolyl Methyl Ether, and on Orcinol Dimethyl Ether.*—Many attempts were made to bring about reaction between these three compounds and aldehydes, ethyl oxalate and alkyl nitrite in presence of agents such as sodium, potassium,



potassium ethoxide, and sodamide, with some expectation that the methylene group of the acetal and the methyl group attached to the nucleus in the two ethers would exhibit reactivity. Only traces, if any, of products with the characters expected were isolated. The significance of these uniformly negative results is referred to in the introductory section of this paper.

The authors' thanks are due to the Department of Scientific and Industrial Research for grants (to L.H. and C.S.) which enabled this work to be done.

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### CCCXL.—The Isoelectric Condition of Gelatin.

By SIDNEY OWEN RAWLING and WALTER CLARK.

ACCORDING to the theory of amphoteric electrolytes as put forward by Michaelis it is readily shown that at the isoelectric point the concentration,  $C_H$ , of hydrion is given by the relation

$$C_H = \sqrt{(K_a K_b / K_w)}$$

where  $K_a$  and  $K_b$  are the acid and basic dissociation constants of the amphoteric electrolyte and  $K_w$  is the ionic product of water (compare Pauli's "Colloid Chemistry of the Proteins," p. 41). Consequently, the hydrion concentration at the isoelectric point should, at a given temperature, be a constant, quite independent of the dilution of the amphoteric electrolyte. Pauli and Samec's experiments (Pauli, *op. cit.*, p. 38) on the precipitation of serum-albumin by alcohol from solutions buffered by sodium acetate-acetic acid mixtures do actually show that the hydrion concentration of the point of maximum precipitation is independent of the concentration of the protein over a considerable range (0.2–1.0 per cent. of albumin). Similar results have been obtained by Michaelis and by Pauli and Samec in electrophoresis experiments (Pauli, *op. cit.*, p. 41).

Theory further shows that at the isoelectric point the undissociated fraction of the ampholyte, that is, the ratio of the number of electrically neutral particles to the total concentration, is at a maximum (Pauli, *op. cit.*, p. 31). The results of numerous experiments indicate that the occurrence of a maximum number of neutral particles will be expressed by a minimum (or maximum \*)

\* In the case of precipitation by alcohol, the amount of precipitate is a maximum at the isoelectric point. \*

in the curve showing the relation between viscosity (or some other physical property) and hydron concentration. Pauli and Matula (*Trans. Faraday Soc.*, 1913, 9, 34; *Kolloid Z.*, 1913, 12, 222) found that for a 1 per cent. gelatin solution at 35°, buffered with sodium acetate-acetic acid mixtures, this minimum occurs at  $p_H = 4.7$ , which agrees with the hydron concentration of the isoelectric point of gelatin as determined by electrophoresis, also in buffered solutions (Michaelis and Grineff, *Biochem. Z.*, 1921, 41, 373).

This value of  $p_H = 4.7$  for the point where solutions of gelatin show a minimum or maximum with respect to some particular physical property has often been confirmed in recent years, a number of different acids having been used to impart definite hydron concentration to the various solutions. For example, Loeb states: that for 0.5, 1.0, and 2.0 per cent. solutions of gelatin hydrochloride the relative viscosity is a minimum at the isoelectric point,  $p_H = 4.7$  (*J. Gen. Physiol.*, 1921, 3, 827); that the viscosity and swelling curves of 1 per cent. solutions of gelatin show a minimum at  $p_H = 4.7$  (*ibid.*, 1918—19, 1, 363); that the swelling is a minimum at the isoelectric point,  $p_H = 4.7$ , for 1 per cent. gelatin solutions containing nitric, hydrochloric, trichloroacetic, phosphoric, oxalic, sulphuric, tartaric, and citric acids respectively (*ibid.*, 1920, 3, 247). In fact, all through his many papers, Loeb states repeatedly that the various physical properties of gelatin solutions show a minimum value at  $p_H = 4.7$ . Similarly Miss Lloyd's results for the swelling of gelatin in hydrochloric acid solution (*Biochem. J.*, 1920, 14, 147) indicate a minimum at  $p_H = 4.7$  (compare Atkin, *J. Soc. Leather Trades Chem.*, 1920, 4, 248). Other evidence has been adduced by Bogue (*J. Amer. Chem. Soc.*, 1922, 44, 1343; *J. Ind. Eng. Chem.*, 1922, 14, 22; *J. Franklin Inst.*, 1922, 193, 795), etc.

Since the same minimum point is obtained irrespective of the acid used, one would conclude that gelatin behaves in the same way towards both strong and weak acids, at all events in the low acid concentrations which are necessary to bring the solution to, or near to, the isoelectric point. The results of Wintgen and Krüger (*Kolloid Z.*, 1921, 28, 81) and Wintgen and Vogel (*ibid.*, 1922, 30, 45) indicate also that towards hydrochloric acid gelatin acts as a mono-acid base (compare also Lloyd and Mayes, *Proc. Roy. Soc.*, 1922, [B], 93, 69).

In practically all the experiments where single acids were used instead of buffer mixtures, attention has been directed only to the hydron concentration produced in the protein solution and to the corresponding value of a particular physical property, and, as seen from the results already quoted, the minimum point in, for example, the viscosity curves of gelatin occurs at the same  $p_H (= 4.7)$  for

different concentrations of the proteins, thus agreeing with the results obtained in buffered solutions. In these experiments with non-buffered solutions, no account seems to have been taken of the quantity of acid which was necessary to produce, for example, a minimum viscosity at various concentrations of gelatin, it apparently being assumed, in accordance with theory, that this quantity is independent of the concentration of the ampholyte (compare Pauli, *op. cit.*, p. 41). Pauli and Samec (*ibid.*, pp. 42–43) have investigated this point by studying the viscosity curves for gelatin and the alcohol precipitation of serum-albumin. The results obtained for the viscosities of gelatin in the presence of sulphuric acid at 35° are given in the following table, where  $t$  and  $t_0$  are the times of flow of the solution and of an equal volume of water respectively through the viscometer, that is,  $t/t_0$  is the relative viscosity.

TABLE I.

Concentration of acid.	1.09% Gelatin. $t/t_0$ .	0.659% Gelatin. $t/t_0$ .	0.33% Gelatin. $t/t_0$ .
0	1.485	1.218	1.113
$5 \times 10^{-4}$	—	1.241	1.111
$1 \times 10^{-4}$	1.453	1.237	<i>1.109</i>
$2 \times 10^{-4}$	1.445	1.233	1.111
$2.5 \times 10^{-4}$	<i>1.443</i>	1.234	1.113
$4 \times 10^{-4}$	1.448	1.241	1.118
$5 \times 10^{-4}$	1.453	1.245	

The minimum viscosities are printed in italics, and, assuming that the measurements are to be trusted to the third place of decimals, it will be seen that as the concentration of the gelatin increases the concentration of acid necessary to produce a minimum viscosity also increases. Similar results were obtained in the precipitation of albumin by alcohol. If these points of minimum viscosity have the same  $p_H$ , agreeing with that of the isoelectric point, then the results are not in accord with theory. Pauli and Samec give no record of the  $p_H$  measurements, so we have repeated their experiments, at the same time measuring the  $p_H$  of solutions of minimum viscosity. Our results (see experimental part) are in agreement with theirs, and, in addition, it is found that the  $p_H$  is the same ( $= 4.7$ ) for all solutions of minimum viscosity. Experiments made with acetic acid in place of sulphuric acid gave similar results.

Because of the discrepancy between theory and experiment the question was reconsidered from the point of view of Sir James Walker's theory of amphoteric electrolytes (*Proc. Roy. Soc.*, 1904, [4], 73, 155). For the sake of simplicity, the external acid added to the gelatin solution is supposed to be a strong, monobasic acid.

If gelatin be considered as a simple amphoteric electrolyte, it

may be represented by the formula  $HXOH$ . Let an external acid, denoted by the formula  $HA$ , be added to the solution. The individuals in the solution will then be :

$H^+$ ,  $OH^-$ ,  $XOH^+$ ,  $XH^+$ ,  $HXOH$ ,  $X$ ,  $A^+$ ,  $HA$  at the respective concentrations  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ ,  $g$ ,  $h$ .

A salt of gelatin,  $HXA$ , with the acid will also be formed, but it has been shown by Manabe and Matula (*Biochem. Z.*, 1913, 52, 369) that when hydrochloric acid up to a concentration of 0.05*N* is added to a 1 per cent. solution of gelatin, the salt formed may be considered as completely dissociated, and in this discussion of the effect of adding acid to gelatin the concentration of the undissociated salt is neglected.

The conditions governing the equilibrium in the solution are expressed by the following equations :

$$ab = K_w \quad . \quad . \quad . \quad (1) \quad \text{whence } b = \frac{K_w}{a}$$

$$ac = K_a e \quad . \quad . \quad . \quad (2) \quad c = \frac{K_a e}{a}$$

$$bd = K_b e \quad . \quad . \quad . \quad (3) \quad d = \frac{K_b ea}{K_w}$$

$$cd = Qf^2 \quad . \quad . \quad . \quad (4) \quad f = \sqrt{\frac{cd}{Q}} = e \sqrt{\frac{K_a K_b}{K_w Q}}$$

$$ag = Kh \quad . \quad . \quad . \quad (5) \quad h = \frac{ag}{K}$$

$$a + d = b + c + g \quad . \quad . \quad (6) \quad \text{for electrical neutrality}$$

where  $K_w$  is the ionic product for water,  $K_a$  the acidic dissociation constant for the amphoteric electrolyte,  $K_b$  the basic dissociation constant for the amphoteric electrolyte,  $K$  the dissociation constant of the acid added, and  $Q$  is a constant.

Substituting in equation (6) for  $b$ ,  $c$ , and  $d$ , we have

$$a + \frac{K_b ea}{K_w} = \frac{K_w}{a} + \frac{K_a e}{a} + g$$

$$\text{whence} \quad g = \frac{K_w}{a} + e \left( \frac{K_b a}{K_w} - \frac{K_a}{a} \right),$$

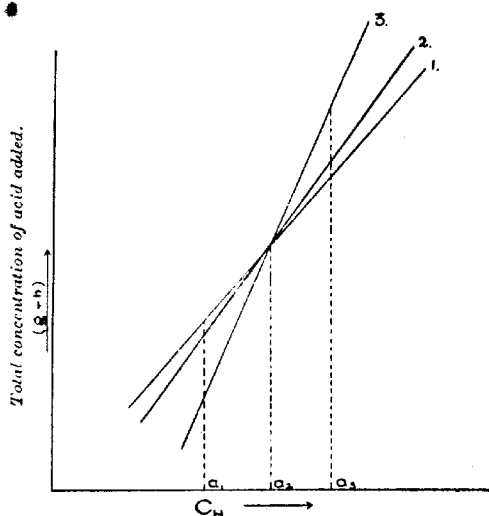
that is to say,  $g$  is a straight-line function of  $e$  for any particular value of  $a$ , and therefore  $(g + h)$ , which expresses the total amount of external acid present per litre, is also a straight-line function of  $e$ , since  $h = ag/K$ .

At the isoelectric point,  $c$  becomes equal to  $d$  (according to definition) and the expression within the bracket becomes zero, that is, the amount of external acid to be added in order to bring the solution to the isoelectric point is independent of any factor connected with the concentration of the ampholyte.

If the concentration of hydron,  $a$ , is less than that which obtains at the isoelectric point, the expression within the bracket will be negative, that is to say, the amount of external acid to be added in order to make the value of  $a$  less than that which holds at the isoelectric point will be smaller as  $e$  increases. On the other hand, for values of  $a$  greater than that of the isoelectric point,  $(g + h)$  increases as  $e$  increases.

In the above deductions  $e$  may be replaced by the total concentration of the ampholyte for any given value of  $a$ , since  $e$  is then

FIG. 1.



proportional to the total concentration, as may be seen from the following :

The total concentration of ampholyte is

$$c + d + e + f = K_a e / a + a K_b e / K_w + e + e \sqrt{(K_a K_b / K_w Q)} \\ = \text{const.} \propto e \text{ for a given value of } a.$$

It follows that for solutions of an ampholyte, acting simply as a monoacid base and a monobasic acid, to which an external acid is added, if we plot total concentration of acid present against the hydron concentration of the solution for various concentrations of ampholyte, a series of curves should be obtained which intersect at a value of  $a$  corresponding with the isoelectric point of the

ampholyte. In the diagram,\* Fig. 1, the curves are numbered 1, 2, and 3 to indicate increasing concentration of ampholyte. To obtain a hydron concentration,  $a_1$ , more acid is required for solution 1 than for solutions 2 and 3. The value  $a_2$  corresponds with the isoelectric point, and at this point the amount of acid is independent of the concentration of ampholyte. For  $C_H$  of  $a_3$  the curves have crossed, and it requires more acid for a greater concentration of ampholyte.

This appears to be the principle of Sørensen's method (*Z. Physiol. Chem.*, 1918, **103**, 192; compare Pauli, *op. cit.*, p. 52) of determining the isoelectric points, but his method of deduction is much more complicated than that given here. It should also hold for a dibasic acid such as sulphuric acid and also for weak acids; in fact, Sørensen uses it for determining the isoelectric point of egg albumin in the presence of a mixture of sulphuric acid and ammonium sulphate, which he considers to be mixtures of the acid  $H(NH_4SO_4)$  with the salt  $NH_4(NH_4SO_4)$ .

The experimental results obtained with gelatin and sulphuric and acetic acids do not agree with this theory, since the amount of acid necessary to give minimum viscosity and a  $p_H$  of 4.7 increases as the concentration of the gelatin increases. It remains to find an explanation for this.

Pauli (*op. cit.*, pp. 45—46) states that in gelatin-hydrochloric acid mixtures the hydron concentration at which non-preferential migration of the protein occurs in electrophoresis experiments is far below that at which the same condition occurs with regulator (buffer) mixtures. From this and other evidence, he concludes that strong acids behave differently from weak acids towards proteins. Examination of his results shows, however, that he really finds that strong acids differ from regulator mixtures, since the action of weak acids alone, that is, not in the presence of their sodium salts, was not investigated. Our results show that acetic acid gives the same anomalies as sulphuric acid. Also the many results of Loeb and others show that when strong and weak acids which dissociate into two ions are compared at the same  $p_H$  they have the same effect, and that dibasic and monobasic acids have similar effects, although the quantitative results are different.

Pauli explains the anomalies to which he directs attention by assuming that in the presence of strong acids certain basic groupings in the protein molecule are brought into action which are not affected by weak acids or by regulator mixtures. It is plausible that such a difference may exist between the action of strong acids

\* The curves may not be straight lines actually, but the diagram is only meant to illustrate the particular point at issue.

and regulator mixtures, owing to the presence of the neutral salt in the latter, but it is difficult to see why there should be a difference in kind rather than in degree between the action of strong and weak acids. If this difference of degree is accepted, the observed behaviour of sulphuric and acetic acids can be explained; \* more of the sulphuric acid than of the acetic acid will be used up in making active the extra basic groupings, but owing to the smaller dissociation of the acetic acid more of it will be necessary than of the sulphuric acid to produce the effect which leads to the isoelectric condition. The actual quantities of sulphuric and acetic acids necessary to give minimum viscosity and the same  $p_H$  may therefore conceivably be approximately the same, as in our experiments.

In working with gelatin, it must be remembered that it is very probable that we are dealing, not with a pure substance, but with a mixture of a protein and its degradation products. Suppose we have a mixture of two ampholytes, the one of which has its isoelectric point at 4.7 and the other at 8.0, and that the amount present of the former is greatly in excess of the latter. It seems probable that when submitted to electrophoresis such a mixture will show equal and opposite electro-diffusion (as measured by Kjeldahl estimations †) at a  $p_H$ , not of 4.7, but of some higher value (lower hydron concentration). In this case, the isoelectric point, as determined by electrophoresis, would be of a  $p_H$  intermediate between the isoelectric point of the ingredients. This would explain Pauli's results with gelatin-hydrochloric acid mixtures, especially since he used gelatin which had been dialysed for a very considerable time, and in which degradation products would be present, but it would not explain an isoelectric point of 4.7 with regulator mixtures.

Consider now the case of minimum viscosity in our hypothetical mixture. The minimum viscosity is supposed to occur when the maximum number of neutral particles is present and this condition with a simple ampholyte occurs at its isoelectric point.

The state of affairs existing in our mixture may be indicated diagrammatically (Fig. 2).

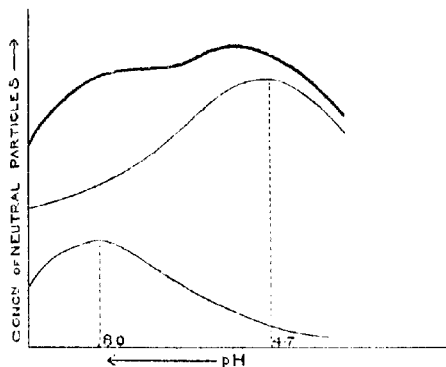
The concentration of neutral particles due to each ampholyte is plotted against  $p_H$  and the sum, shown by the thick curve, gives the total concentration of neutral particles. Again the maximum occurs between the isoelectric points. Von Schroeder (*Z. physikal. Chem.*, 1903, 45, 75) has shown that the viscosity of the degradation

\* Pauli and Hirschfeld (*Biochem. Z.*, 1914, 82, 245) found that for a given concentration of acid more sulphuric than acetic acid is bound by albumin.

† Total nitrogen estimations alone do not in any way tell us the nature of the diffusing material.

products of gelatin is much lower than that of undegraded gelatin and therefore, in the case of gelatin, it is reasonable to assume that the viscosity will be more affected by the neutral particles of the unhydrolysed protein than by even an equal concentration of such particles of the degradation products. The viscosity minimum of the mixture would therefore most likely occur much nearer to the isoelectric point of the unhydrolysed protein than to that of the degradation products; it may practically coincide with the isoelectric point of the undegraded gelatin, as is actually found to be the case. The non-coincidence of the point of equal and opposite electrophoresis with that of minimum viscosity in the case of strong acids may thus be explained.

FIG. 2.



## EXPERIMENTAL.

The gelatin used throughout these experiments was very kindly supplied by Drs. Mees and Sheppard of the Kodak Research Laboratory. It had been prepared by electrophoresis methods as described by Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, **44**, 1858) and was stated to contain not more than 0.1 per cent. of ash; \* our analyses confirmed this statement.

The solutions of which the viscosities were to be measured were made as follows. The amount of gelatin required to give 100 c.c.

\* Gelatin which is practically ash-free, and which is often prepared by methods depending on first obtaining an isoelectric solution of gelatin, seems to be commonly spoken of as *isoelectric* gelatin. This is a misnomer, since theoretically, isoelectric gelatin can only exist in a solution containing extra hydron supplied by an external acid. Such gelatins should always be spoken of as ash-less or ash-free gelatins.



of a solution of definite strength (calculated as moisture-free gelatin) was weighed out into a 100 c.c. flask. About 75 c.c. of freshly boiled and cooled distilled water were added and the whole was then heated in a water-bath from room temperature to 75° in twenty minutes (compare Davis, Oakes, and Brown, *J. Amer. Chem. Soc.*, 1921, **43**, 1526). In the cases where acid was added, the addition was made at this point in the procedure. The volume of the solution was then made up to 100 c.c. with water at 75° and the solution quickly filtered by the aid of the pump, using hardened filter-paper. The filtered solution was placed in a flask in the thermostat at 35.4° and a sample pipetted into the viscometer held ready in the same bath.

For measuring the viscosities, a capillary viscometer of the Ubbelohde type, working under a constant head of pressure, was used (compare Hatschek, "Laboratory Manual of Elementary Colloid Chemistry," pp. 100—103; Hess, *Kolloid Z.*, 1920, **27**, 154). The viscometers were carefully calibrated with water at 35.4°. In the case of two of them, the times of flow with water were 64 and 82.2 seconds, respectively, using a head of pressure of 34.9 cm. of water. Experiments made with a different head of pressure, using the quicker-running instrument, showed that errors due to eddy currents did not occur, and therefore were much less likely to occur with gelatin solutions. For example, with a head of pressure of 20 cm. of water the product of pressure and time of flow was the same as that obtained for a pressure of 34.9 cm. In order to eliminate errors as far as possible, the same viscometer was used for the whole of any one series of measurements. Unfortunately, owing to breakages, which readily occur during cleaning, it was not possible to use the same viscometer for all the series.

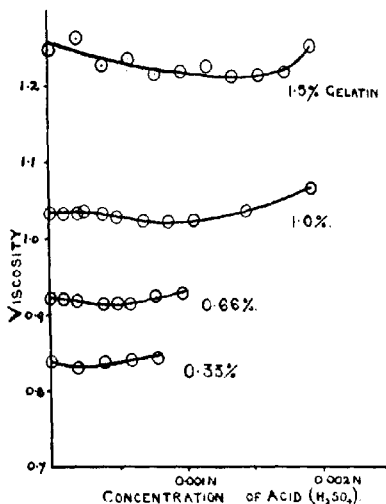
A temperature in the neighbourhood of 35° was chosen for the measurements in order that the viscosity of the solutions should not alter on keeping for some time in the thermostat, and also for comparison with Pauli and Samec's results. In this way it was possible to make several observations of the time of flow with the same solution. For example, the same 1 per cent. gelatin solution at 12.30, 1.35, and 1.57 p.m. gave times of flow of 106.1, 106.2, and 106.2 seconds, respectively. Boguc's figures (*J. Amer. Chem. Soc.*, 1922, **44**, 1319) for a 2 per cent. solution at 35° also show that for a range of  $p_H$  values such as those used in this investigation the viscosity values do not vary over an interval of two or three hours.

The results obtained for 1.5, 1.0, 0.66, and 0.33 per cent. solutions, containing sulphuric acid, are given in Table II, the viscosities being expressed in centipoises. The curves showing the relation between

the viscosity and the concentration of acid in the solution are given in Fig. 3.

In the neighbourhood of the minimum point, the viscosity changes very little with alterations in the amount of acid added to the solution. The experimental method used does not permit of a greater accuracy than about 0.3 per cent., so that in repetition measurements it is possible to obtain figures which indicate either a minimum or else a region of practically non-varying viscosity. If such variations did occur, however, it was found that any minimum indicated in one experiment always occurred in the region

FIG. 3.



of non-varying viscosity obtained in repetition experiments. By comparison of the various results, the positions of the minima have been fixed, it is believed, within an accuracy of about 1 c.c. of *N*/100-acid. The minima are indicated by being printed in italics.

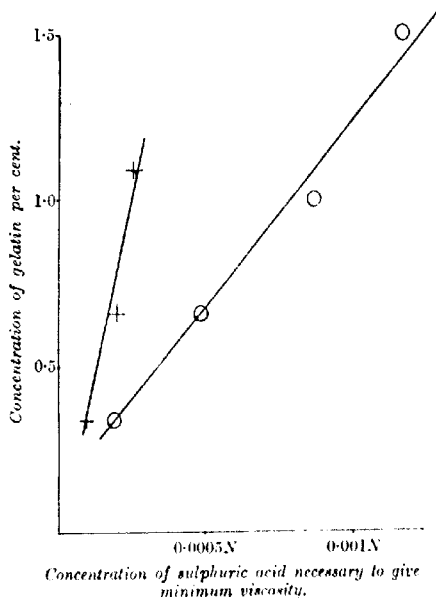
The results obtained are thus very similar in type to those of Pauli and Samec, although, if they are plotted as in Fig. 4, it will be seen that they do not agree, probably because different kinds of gelatin were used. Our results further indicated that the amount of acid necessary to give a solution with minimum viscosity varies directly with the concentration of the gelatin, but it would be premature to take this relation as proved.

In contradistinction to Pauli and Samec, measurements of the

hydron concentration of solutions showing a minimum viscosity and also of some other solutions have been made. Hydrogen electrodes of the type employed by Lloyd and Mayes (*loc. cit.*) were used, and in every case determinations were made with two different and freshly prepared electrodes. The point only of each electrode was allowed to touch the solution, and measurements were made as soon as possible after contact. It will be seen (Table II) that in

FIG. 4.

Points represented by circles are values taken from Table II; those represented by crosses are values obtained by Pauli and Samec, Table I.



each case the solution showing minimum viscosity has a  $p_{H}$  of 4.6–4.7, that is, the isoelectric point is independent of the concentration of the gelatin. Loeb's measurements were generally made at 20° or 24°, and in all cases he found 4.7 as the  $p_{H}$  of the isoelectric point. The value seems to be the same at 35°, but it would only be safe to say that within the limits of error of experiment the value remains the same over the temperature interval indicated. Davis and Oakes (*J. Amer. Chem. Soc.*, 1922, 44, 478) find that at 40° the minimum value of the viscosity for 1 per cent.



solutions is at  $p_H$  8.0, but this anomaly requires further investigation.

The results obtained for the viscosities of gelatin solutions were repeatedly checked, but it was thought advisable to carry out a new series of measurements, making up the solutions in a different way. A stock solution of 2 per cent. strength was made by dispersing the gelatin in water at  $70^\circ$ , and, after filtering, was placed in the thermostat at  $35.4^\circ$ . Fifty c.c. were then pipetted into a 100 c.c. graduated flask and diluted to the mark with water and the required amount of dilute acid. The diluted solution was then heated to  $70^\circ$ , in order rapidly to attain equilibrium after diluting (compare Arisz, *Koll. Chem. Beihefte*, 1915, 7, 1), and again placed in the thermostat, the viscosity then being measured when the temperature had reached  $35.4^\circ$ . Solutions of 0.66 and 0.33 per cent. strength were similarly prepared. This method of preparation will give slightly weaker solutions than those of the corresponding strength made by the first method, so that the viscosities will be somewhat lower. This is of no importance, however, since the object of the experiments was simply to find the connexion between the hydron concentration and the minimum viscosity; the method has the advantage of using the same sample of gelatin for each series of measurements, and it is well known that gelatin is a very difficult substance to sample satisfactorily.

The results are given in Table II under the heading "Method 2" and it will be seen that they agree with those found by the first method.

Table III gives the results of measurements made when acetic acid was used, and it will be seen that the quantities of acid necessary to produce a minimum viscosity are approximately the same as those of sulphuric acid.

TABLE III.  
Acetic acid and gelatin.

Concentration of acid.	Viscosities (first method only).		
	1% gelatin.	0.66%.	0.33%.
0	1.042	0.942	0.8375
$2 \times 10^{-4}$	1.020	0.933	0.830
$4 \times 10^{-4}$	1.005	0.933	0.838
$6 \times 10^{-4}$	1.005	0.942	0.840
$8 \times 10^{-4}$	1.002	0.946	0.843
$10 \times 10^{-4}$	1.002		
$12 \times 10^{-4}$	1.006		
$14 \times 10^{-4}$	1.008		

In 1 per cent. solution in which the concentration of acetic acid was  $9 \times 10^{-4}$  the  $p_H$  was 4.65.

In accordance with theory, it was further found that when a solution of gelatin, made isoelectric ( $p_H = 4.7$ ) either with acetic or sulphuric acid, was diluted to twice or three times its volume its  $p_H$  remained constant within the errors of measurement.

*Summary.*

1. The minimum viscosity of gelatin sols occurs at a  $p_H$  of 4.7 at 35.4° with both strong and weak acids.
2. The amount of acid required to produce the minimum viscosity in a given volume of gelatin sol is not independent of the concentration of gelatin, but appears to be a straight-line function of it.
3. The amount of sulphuric acid required to produce minimum viscosity is approximately the same as the corresponding amount of acetic acid.
4. The fact that in some cases the point of non-preferential wandering of protein under the action of an imposed *E.M.F.* occurs at a  $p_H$  above that at which minimum viscosity occurs may be due to the presence of basic degradation products of the protein.

The authors are indebted to Dr. T. Slater Price, at whose suggestion this work was undertaken, for much valuable criticism and advice.

LABORATORIES OF THE BRITISH PHOTOGRAPHIC RESEARCH ASSOCIATION.

[Received, November 4th, 1922.]

### CCCXLI.—*The Adsorption of Radium-B and Radium-C by Ferric Hydroxide.*

By JOHN ARNOLD CRANSTON and ROBERT HUTTON.

It has been shown that ferric hydroxide adsorbs thorium-B and thorium-C in proportions varying regularly with the acidity of the solution (Cranston and Burnett, T., 1921, 119, 2036). When the acidity was plotted against the atomic ratio Th-B/Th-C adsorbed, a curve was obtained having an inflexion at a point corresponding with the radioactive equilibrium ratio of thorium-B to thorium-C.

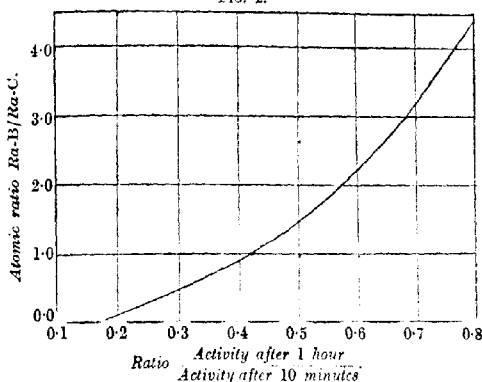
It appeared important to find out whether a mixture of their isotopes, radium-B and radium-C, respectively, behaved in a similar manner, showing a point of inflexion corresponding with the same ratio, or whether a point of inflexion occurred corresponding with the different equilibrium ratio of radium-B to radium-C. This has now been done and the latter found to occur.



ratio against the ratio  $Ra-B/Ra-C$ . The latter curve is shown in Fig. 2.

The experiment was carried out in the following manner. A colloidal solution of ferric hydroxide was prepared by adding 3 c.c. of *N*-ferric chloride solution to 300 c.c. of distilled water which had been heated to boiling. The solution was then dialysed free from hydrochloric acid. An active deposit was obtained on a platinum wire in the usual way and dissolved by addition of acid of the required strength. The solution was kept for half an hour so that the effect of the radium-*A* would be negligible, and the radium-*B* and radium-*C* would be more nearly in radioactive equilibrium.

FIG. 2.



In carrying out the adsorptions, 2 c.c. of the colloidal solution were added to the solution of the active deposit in the required strength of acid. The ferric hydroxide was then precipitated by adding a drop of sodium sulphate solution. The precipitate was rapidly filtered and dried and the activity determined at short intervals in the  $\alpha$ -ray electroscope. The zero time for the curves was that at which the colloid was added to the solution of the radioactive elements. The actual decay curves obtained are shown in Fig. 3, the scale of the activities being chosen so that the initial activity in each case is 100.

For acidities lower than 0.0001*N* the hydrochloric acid was replaced by mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate for which the hydrogen-ion concentration was known. The acidities were checked by determining the hydrogen-ion concentration in the filtrates by means of the hydrogen concentration cell.



The results are shown in the following table, the hydrogen-ion concentration being expressed as  $-\log [H^+]$ .

$-\log [H^+]$ .....	2.0	2.7	3.0	3.4	3.7	4.0	5.2	6.2	6.9	7.8
Atomic ratio .....	0.18	0.15	0.15	0.16	0.5	0.8	1.05	2.05	1.85	1.76

FIG. 3.

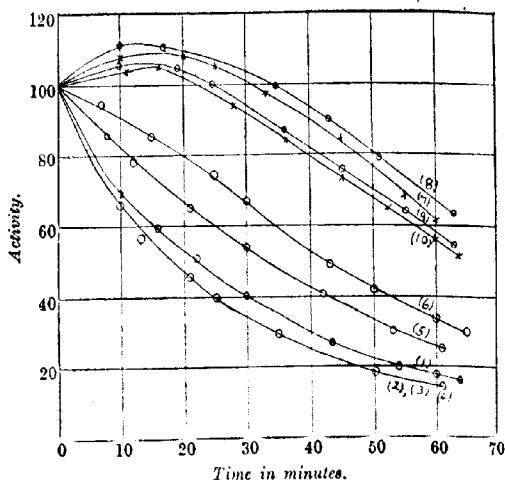
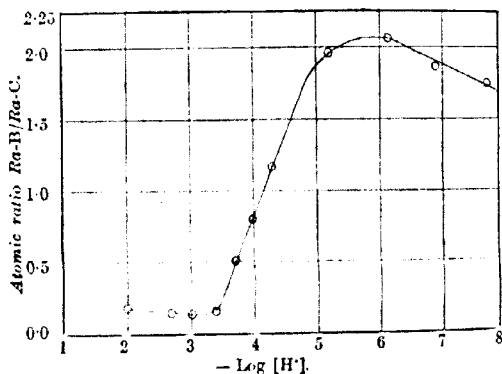


FIG. 4.



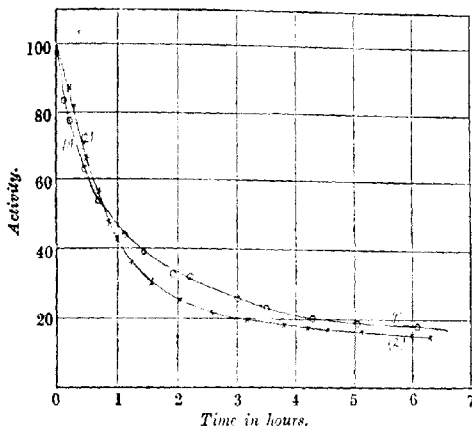
The value of  $-\log [H^+]$  was plotted against the atomic ratio  $Ra-B$  to  $Ra-C$  adsorbed. The curve obtained is shown in Fig. 4. It thus appears that the ratio of  $Ra-B$  to  $Ra-C$  adsorbed at a definite

acidity is different from the ratio of their isotopes, Th-B/Th-C, adsorbed at the same acidity.

Experiments were then carried out on the simultaneous adsorption of the four elements, Ra-B, Ra-C, Th-B, and Th-C. Since a marked difference exists between the decay curves of the two series, it was thought that the respective ratios Ra-B/Ra-C and Th-B/Th-C could be found from the experimental curve obtained when both series are decaying.

The active deposit of thorium was obtained on a platinum plate and the radium active deposit on a platinum wire. The deposits were dissolved off in 0.001N-hydrochloric acid and the solutions

FIG. 5.



mixed and left for half an hour. Previous experiments had shown that under these conditions thorium-B and thorium-C, as well as radium-B and radium-C, would be present in approximately equilibrium ratio. The adsorption was carried out exactly as before. Fig. 5 shows the experimental curves obtained.

A series of theoretical decay curves were plotted for Th-B/Th-C in a similar manner to those for Ra-B/Ra-C. They are shown in Fig. 6. From the initial rate of decay of the experimental curve (Fig. 5), it was assumed that the activity after three hours would be due entirely to the thorium members, the effect due to the radium-C being then negligible. Thus from the reading at the end of three hours and at the end of six hours, it was possible by comparison with the theoretical curves to determine the ratio of thorium-B to thorium-C originally adsorbed, and hence their

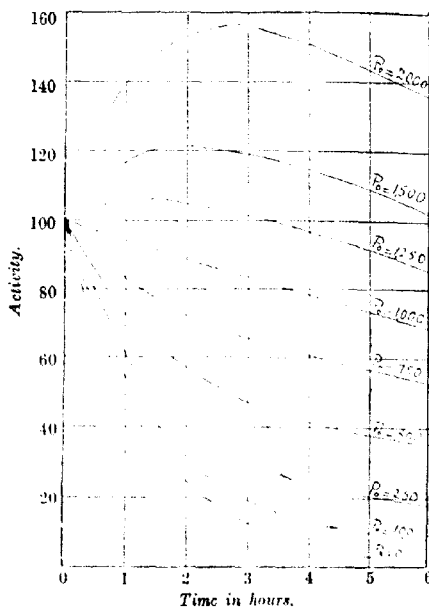
initial activity. The difference curve thus obtained was due to the radium members.

In this manner, the curves of Fig. 5 were found to correspond with the following ratios.

	Expt. 1.	Expt. 2.
Ratio Ra-B/Ra-C adsorbed .....	0.18	0.2
Ratio Th-B/Th-C adsorbed .....	4.1	4.8

Thus from the same solution the ratio of elements of atomic number 82 and 83 adsorbed has a different value according to the

FIG. 6.



series to which the elements belong; or, in other words, a partial separation of isotopes has been effected.

In order to avoid the conclusion that isotopic elements have not similar adsorptive properties, the authors conclude that the evidence obtained is in support of the colloidal theory put forward in the paper already referred to. They picture in 0.001N-acid solution a certain proportion of the -B members as existing in the state of colloidal aggregates of negative charge which, with lapse of time, disintegrate partially into the -C members. These are held in the

colloidal state and are adsorbed owing to the predominating influence of the remainder of the *B* members. Hence the adsorption of the *C* members is in greater proportion for the radium series owing to the period of radium-*B* being less than that of thorium-*B*.

Further experiments are being carried out to determine quantitatively the influence of the relative concentrations of the *B* and *C* members before adsorption on the ratio in which they are adsorbed.

#### *Summary.*

1. Previous work on the adsorption of *B* and *C* members by ferric hydroxide has been continued. Radium-*B* and radium-*C* are adsorbed in proportions varying regularly with the acidity of the solution.

2. At a given acidity the ratio Th-*B*/Th-*C* adsorbed is greater than the ratio of Ra-*B*/Ra-*C* adsorbed.

3. This different behaviour is maintained when the adsorption is carried out in a mixed solution of the four radio-elements.

4. These results are interpreted as evidence in favour of the colloidal theory put forward in a previous paper.

The authors are indebted to The Glasgow and West of Scotland Radium Committee for supplying quantities of radium emanation from which the active deposits were prepared.

ROYAL TECHNICAL COLLEGE,  
GLASGOW.

[Received, November 11th, 1922.]

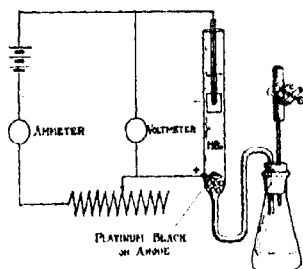
### CCCXLII.—*The Hydrolysis of Platinum Salts. Part II.* *Potassium Platinibromide.*

By EBEN HENRY ARCHIBALD and WILLIAM A. GALE.

CERTAIN features regarding the hydrolysis of potassium platinichloride have been noted by one of us in a previous paper (T., 1920, 117, 1104), where the extent and rapidity of the reaction, under definite conditions as to temperature and intensity of light, have been described. In particular, it was found that a solution as dilute as  $N/100$  ( $K_2PtCl_6$  400) did not undergo hydrolysis in the absence of light radiation, within, at least, several months from the time of preparation; whilst with a  $N/50$ -solution the hydrolysis would begin in the absence of light after several days and then proceed to the same equilibrium point as when under the influence of strong light radiations. When soluble chlorides were added to the solution of the hydrolysed salt, the reverse of the previous

reaction appeared to begin at once, and, if sufficient chloride had been added to give approximately a  $N/10$ -solution, the reverse reaction continued until the acidity of the solution disappeared. There were some indications of a secondary reaction taking place after the hydrolysis had reached the point of maximum acidity, without the influence of any added common ion, a secondary reaction that lowered the acidity, but the effect was so small that it could not be measured with certainty. A few preliminary experiments showed that this secondary reaction was much more marked in the case of the platinibromide, and as a study of this change in the solution might be expected to throw some light on the main reaction, it was thought worth while to follow the decomposition of the platinibromide as we had done for the platinichloride. There was, further, the question as to whether the intensity of the light

FIG. 1.



would influence the final equilibrium point of the solutions; a study of the behaviour of the bromide might throw some light on this point. With these features of the problem in mind, the experiments described below were carried out.

#### EXPERIMENTAL.

*Preparation of Materials.*—The same care was taken in the preparation of all the chemicals used as in the previous investigation. The methods used in the purification need not be repeated here. In preparing the potassium platinibromide, the method employed was very similar to that used in the case of the platinichloride. A strong solution of hydrobromic acid was electrolysed, using as anode the purified platinum black. The arrangement of the apparatus will be easily understood from Fig. 1.

The solution of bromoplatinic acid which resulted contained a large excess of bromine, and a part of this was expelled before the potassium bromide solution was added in the precipitation of the

TABLE I.

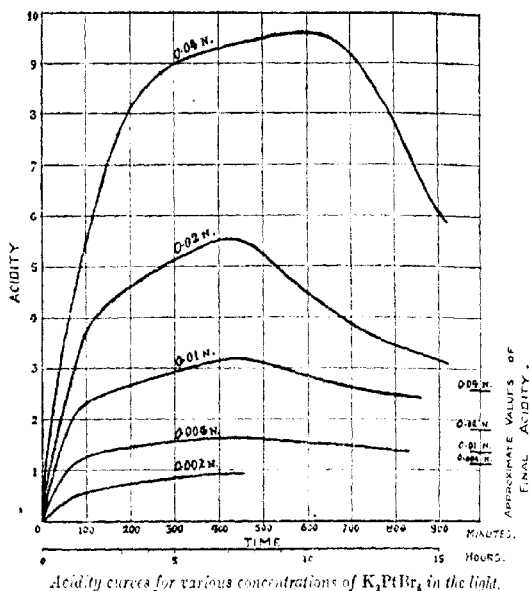
N/500-K <sub>2</sub> PtBr <sub>6</sub> solution.			N/250-K <sub>2</sub> PtBr <sub>6</sub> solution.		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HBr, gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HBr, gram.
0	0	0.00000	0	0	0.00000
30.0	0.30	0.00024	62.0	1.1	0.00089
90.0	0.55	0.00045	89.0	1.3	0.00105
120.0	0.60	0.00049	149.0	1.4	0.00113
215.0	0.75	0.00061	242.0	1.5	0.00121
285.0	0.80	0.00065	337.0	1.6	0.00130
415.0	0.95	0.00077	400.0	1.7	0.00138
			720.0	1.4	0.00113
			Light off { 840.0    1.3    0.00105		
			15 days    1.1    0.00089		
N/100-K <sub>2</sub> PtBr <sub>6</sub> solution.			N/50-K <sub>2</sub> PtBr <sub>6</sub> solution.		
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HBr, gram.	Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HBr, gram.
0	0	0.00000	0	0.03	0.00002
60.0	2.0	0.00162	47.0	2.2	0.00178
85.0	2.3	0.00186	120.0	4.0	0.00324
145.0	2.6	0.00211	365.0	5.6	0.00454
236.0	2.8	0.00227	490.0	5.2	0.00421
332.0	3.0	0.00243	550.0	4.7	0.00381
420.0	3.2	0.00259	Light turned off { 740.0    3.7    0.00300		
537.0	3.0	0.00243			
Light off { 652.0    2.8    0.00227					
			25.3 hrs.    3.0    0.00245		
			42 days    1.9    0.00154		
N/25-K <sub>2</sub> PtBr <sub>6</sub> solution.					
Time, minutes.	Ba(OH) <sub>2</sub> solution, c.c.	HBr, gram.			
0	0.03	0.00002			
58.0	3.3	0.00267			
130.0	6.2	0.00502			
285.0	9.0	0.00729			
368.0	9.2	0.00745			
435.0	9.4	0.00761			
545.0	9.6	0.00778			
			Light turned off { 740.0    8.8    0.00713		
			860.0    6.6    0.00535		
			26 hours    3.8    0.00308		
			49    3.2    0.00259		
			42 days    2.6    0.00211		

platinum salt. The platinibromide was washed with dilute bromide solution and alcohol in a Gooch crucible and carefully dried at a low temperature.

The colour of the product varies appreciably with the size of the crystals formed—that is, with the rapidity of precipitation—from bright scarlet to deep ruby red.

*The Experiments.*—The procedure followed in preparing the solutions of the platinum salts, exposing them to the light radiations, and the subsequent titration of the acid formed from the hydrolysis, were the same as described in the previous paper. With the platinibromide, Congo-red as an indicator was found to give the best results. 1 C.c. of the barium hydroxide solution was equivalent to 0.0081 gram of hydrobromic acid.

FIG. 2.



Acidity curves for various concentrations of  $K_2PtBr_6$  in the light.

The different solutions studied had concentrations corresponding to 0.004N, 0.01N, 0.02N, and 0.04N, considering one-fourth the formula weight,  $K_2PtBr_6 \cdot 4$ , the equivalent.

Table I shows the extent to which the hydrolysis has gone under the influence of light. The time of exposure in minutes is given in the first column. The second column shows the c.c. of barium hydroxide solution necessary to neutralise a 10 c.c. portion of platinum solution, whilst the third column gives the weight in grams of hydrogen bromide formed in 100 c.c. of solution.

The progress of the hydrolysis will be more readily seen from a consideration of the curves shown in Fig. 2, where the time as

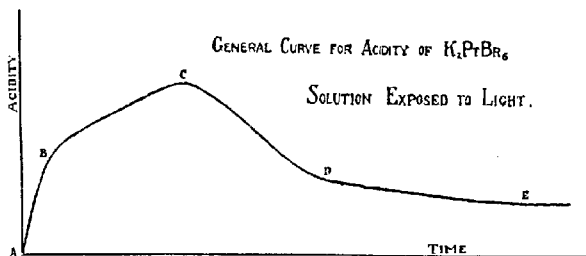
abscissae is plotted against the acidity expressed as the volume of hydroxide solution used for 10 c.c. portions.

The shape of the curve is very much the same for all concentrations studied. It is noteworthy that the rise is at first very rapid, the maximum acidity being attained within seven or eight hours. The drop in the acidity from the maximum which was scarcely noticeable in the case of the platinichloride is here very marked, and continues until almost 40 per cent. of the acid formed has disappeared.

The general curve as shown in Fig. 3, which represents fairly closely the progress of the reactions, at least for the four more concentrated solutions, may be divided into four parts.

From A to B we have the initial rate of hydrolysis where the amount of acid in the solution has not been appreciably affected by any secondary reaction. From B to C we have an almost straight

FIG. 3.



line portion, rising to a maximum at C, in approximately eight hours, with the particular intensity of light used. Over this part of the curve the influence of the reaction which accounts for the disappearance of so much of the acid formed is clearly seen. From C to D the acidity decreases rapidly, whilst from D the decrease is very slow until final equilibrium is reached.

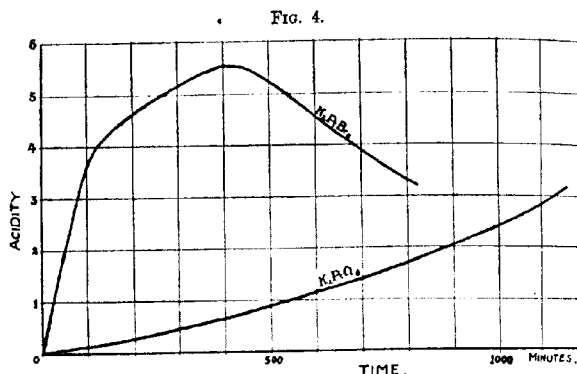
It is found that if a solution that has been exposed to the light be placed in the dark before the acidity corresponding with point B is reached, the hydrolytic reaction practically stops, but will continue again on re-exposure. If point B has been passed before the solution is placed in the dark, the acidity does not remain constant but gradually drops to the point of final equilibrium, almost as rapidly as if in the light. This seems to show that the reverse reaction is not influenced by the light to the same extent as the direct reaction.

The difference in the behaviour of solutions of platinibromide and platinichloride can be seen from the shape of the curves in



Fig. 4. The rate of the hydrolytic reaction is very much greater in the case of the platinibromide solutions, and the point of maximum acidity is reached much sooner for these solutions than for those of the platinichloride. The maximum point, however, for the platinichloride is much higher than for the platinibromide, and there is very little, if any, recession in the case of the former solutions from this maximum, whilst the reverse reaction for the bromide accounts for a considerable decrease in the acidity of the solution and takes place at an appreciable rate.

The fractions of the bromine assumed to be replaced at the point of maximum acidity and of final equilibrium, for the several concentrations, are shown in Table II. The values are expressed as



Comparison of rates of hydrolysis of  $K_2PtBr_6$  and  $K_2PtCl_6$  solutions of equal concentration (0.02N) in the light.

fractions of the bromine associated with the platinum as  $PtBr_4$ . The second and fourth columns give the fraction of one Br that has been replaced for that concentration.

TABLE II.

Normality of solution ( $K_2PtBr_6$ ).	Br replaced at maximum.		Br replaced at final equilibrium.	
	Fraction of 1 Br.	% of 4Br.	Fraction of 1 Br.	% of 4Br.
0.04	0.97	24.25	0.28	6.0
0.02	1.12	28.0	0.36	9.0
0.01	1.28	32.0	0.50	14.0
0.004	1.7	42.5	1.10	27.5
0.002	1.9	47.5	—	—

*Hydrolysis in the Dark.*—The behaviour of the solutions when prepared and kept in the dark was as follows. No change could be detected for the first three days. The acidity then rose slowly

to an equilibrium corresponding with the final acidity reached in the light; there being no evidence of a decrease. The time required to reach this point was about fifteen days, both for a saturated solution and one that was 0.02N.

*The Effect of Adding a Common Ion.*—The addition of potassium bromide to a hydrolysed solution caused a reversal of the reaction, as indicated by a rapid decrease of acidity. A 0.02N-solution that had reached equilibrium in light became neutral in forty minutes in the light after sufficient potassium bromide had been added to give a 0.05N-solution of KBr. The influence of the light on this reverse reaction in the presence of potassium bromide is illustrated by the fact that a solution which required five hours for reversal in the dark only required forty minutes in the light.

The addition of sodium bromide to the hydrolysed solution had a similar effect to that of the potassium bromide, whilst an equivalent amount of potassium nitrate did not appreciably change the point of equilibrium; neither did the presence of potassium nitrate noticeably affect the rate of the hydrolytic reaction if added to the solution undergoing hydrolysis.

*Attempts to Isolate a Product Formed by Hydrolysis.*—An attempt was made to precipitate from the hydrolysed solution a product of the hydrolysis. Thinking that the reaction product was probably less soluble than the original salt, we added a saturated solution of potassium bromide to a solution having a maximum acidity. The bright scarlet crystals which separated were carefully analysed for platinum and potassium bromide, by heating a weighed portion of the precipitate in a porcelain boat in a stream of hydrogen. The platinum black and potassium bromide were weighed, the weights corresponding very closely with the formula  $K_2PtBr_6$ . Evidently no appreciable amount of the product formed by hydrolysis had been precipitated.

Evaporation of a hydrolysed solution also yielded crystals of the normal platinibromide. The weight of the residue corresponded exactly with the weight of potassium platinibromide known to have been originally present. Samples of these crystals as well as some obtained from the precipitation noted above were examined under a high-power microscope and found to have the same form as those of the original compound. These results seem to confirm the supposition that the  $PtBr_6^{--}$  ion is re-formed by the reverse reaction.

A few of the crystals formed from the evaporation were redissolved and the solution was exposed to the light as before; the initial rate of the hydrolysis was the same as before, but the point of maximum acidity was not as high—the B C portion of the curve

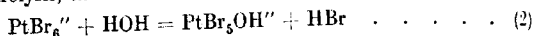
(Fig. 3) being flatter. This was also the case with portions recovered from titration residues by partial evaporation and precipitation with saturated potassium bromide solution. This may be due to the presence of traces of hydrolysed products which act catalytically in the reverse reaction.

To another solution that had reached its point of maximum acidity a considerable quantity of alcohol was added. Again the precipitate obtained proved on examination to be the platinum bromide.

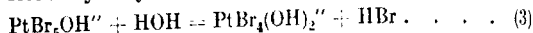
The observed increase and decrease in acidity may be accounted for by assuming that the following chemical reactions take place; we may suppose that the salt in solution is almost completely ionised, thus :



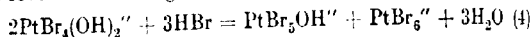
Under the action of light the ion carrying the bromine then undergoes hydrolysis, thus :



The second hydroxyl adds on more slowly than the first one, thus :



The ion  $PtBr_4(OH)_2''$  then reacts with the hydrobromic acid formed and reverts to the original states :



As pointed out above, the experiments show that the light has a much greater effect on the direct than on the reverse reaction. It appears, then, that only in the light does reaction (3) take place rapidly enough to more than counterbalance the effect of reaction (4). In such a case we get the maxima shown in the curves (Fig. 2). In the absence of light radiation, reaction (3) goes so slowly that its effect is entirely masked by that of (4).

Using the spectroscope of a Tutton monochromatic illuminator and Baly absorption tube, some observations have been made of the absorption spectrum of solutions of the platinum bromide. As soon as circumstances will permit we wish to extend these measurements to include both the hydrolysed and unhydrolysed solutions, as well as the corresponding solutions for the platinum chloride.

#### Summary.

(1) Solutions of potassium platinumbromide are rapidly hydrolysed under the influence of light.

(2) The acidity of the solution increases, at first rapidly, then more slowly to a maximum, and finally decreases to an equilibrium that varies with the concentration of the solution.

(3) The addition of a soluble bromide causes complete reversal of the chemical action. The reaction involved here is also accelerated by light.

(4) In the absence of light radiations, hydrolysis can be noticed in the solutions only after several days; the final equilibrium point is then reached without the solution showing a maximum point on the acidity curve.

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CCCXLIII.—*Researches on Residual Affinity and Co-ordination. Part XII. Cobaltamine and Ferric Lakes of Dinitrosoresorcinol.*

By GILBERT T. MORGAN and JOHN EWART MOSS.

In two earlier communications (T., 1921, 119, 704; this vol., p. 160) on cobaltamine lakes of quinoneoxime and alizarin dyes, it was shown experimentally that these adjective dyes owe their distinctive lake-forming properties to the presence in the colour molecule of at least one unsaturated group (I or Ia) capable of



taking up two positions in the co-ordination complex surrounding a metallic atom so that the latter becomes finally held in a heterocyclic ring. To these unsaturated radicles, which are capable of acting as two associating units, has been given the name of chelate groups because of the tenacity of their grip on the implicated metallic atom.

The presence of chelate groups in a dye may be detected by the use of a cobaltamine reagent consisting of an ammoniacal solution of hydroxypentamminocobaltic chloride,  $[\text{HO}\cdot\text{Co}(\text{NH}_3)_5]\text{Cl}_2$ . If the dye contains one chelate group, three of these unsaturated radicles combine with one atom of tervalent cobalt, satisfying completely its principal and supplementary valencies so that the metallic atom loses completely its capacity for combining with ammonia. This central cobalt atom, which is then said to be completely chelated, has become implicated in three heterocyclic rings, one arising from each of the three chelate groups.

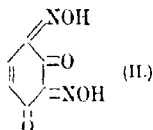
Meanwhile, the cobaltammine reagent combines with any other acidic groups present in the dye to give a pentamminocobaltic salt, so that if the resulting complex lake contains  $n$  atoms of cobalt and  $m$  molecules of ammonia the relationship between these constituents is expressed by equation (i) . . .  $m = 5(n - 1)$ .

If there are two or more lake-forming chelate groups present in the dye, the relationship becomes somewhat more complicated, because, owing to spatial arrangement, the second chelate group can only co-ordinate once with a trivalent cobalt atom, the latter retaining the power of association with four molecules of ammonia. The equation for a polychelate dye thus becomes

$$\text{ii} \quad \dots m = 5 \left[ n - \frac{c + 4}{5} \right],$$

where  $c$  is the number of chelate groups. Several examples of dichelate mordant dyes have been observed in the alizarin series (*loc. cit.*).

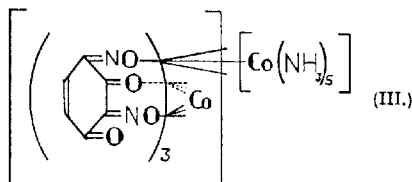
These considerations have now been applied to the case of dinitrosoresorcinol or 1:2:3:4-benzodiquinone-1:3-dioxime (II) with the object of ascertaining the nature of the metallic lakes derived from this quinoneoxime dye, or, in other words, of finding out whether the colouring matter is a monochelate or a dichelate dye. Dinitrosoresorcinol, when precipitated on iron mordants,



gives rise to fast green lakes, variously designated as resorcinol green, chlorin, resorcin green, Alsace green, fast myrtle green, etc. With chromium mordants, it furnishes fast brown lakes. These shades of colour resemble closely those derived from the 1:2-naphthaquinonemonoximes (Gambine or nitrosonaphthol dyes) which have been shown definitely to be monochelate dyes (*loc. cit.*).

The foregoing consecutive formula II assigned to dinitrosoresorcinol has not hitherto been demonstrated by direct proof, but nevertheless this constitution is rendered very probable by the analogies drawn from the behaviour of homologues of resorcinol towards nitrous acid.  $\beta$ -Orcinol [ $2\text{CH}_3:2\text{OH} = 1:4:3:5$ ], in which one methyl group occupies the position contiguous to the two hydroxyl radicles, yields only a mononitroso-derivative even with excess of nitrous acid, whereas orcinol [ $\text{CH}_3:2\text{OH} = 1:3:5$ ] and its isomeride, cresoreinol [ $\text{CH}_3:2\text{OH} = 1:2:4$ ], readily furnish dinitroso-compounds even with a deficiency of nitrous acid, and in

the latter instance one of the nitroso-groups must enter the position contiguous to the two hydroxyl radicles (Kostanecki, *Ber.*, 1887, 20, 3133). The consecutive formula for dinitrosoresorcinol suggests a possibility that this substance may behave towards metallic mordants as a dichelate dye, in which contingency the cobalt-ammine lake should have a composition determined by the second of the foregoing equations. Putting  $c$  and  $n$  each equal to 2, the number,  $m$ , of ammonia molecules should be four. Experiment shows, however, that the dicobaltic lake contains not four but five molecular proportions of ammonia in accordance with equation i. Hence it follows that dinitrosoresorcinol, although a dioxime, behaves as a monochelate dye, thus falling into line with the nitrosonaphthol or 1:2-naphthaquinonemonoxime colouring matters. The simplest explanation of this behaviour is that the median *isonitroso*- and carbonyl radicles form the two limbs of the chelate group, leaving to the terminal *isonitroso*-radicle the simpler function of salt-formation. On this hypothesis, the constitution to be assigned to the cobaltammine lake is as shown in formula III.

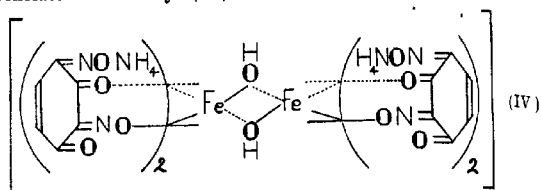


This view of the constitution of the cobaltammine lake is confirmed by evidence derived from a study of the iron lakes of dinitroso-resorcinol.

The iron lakes of quinoneoxime dyes are almost invariably cited as ferrous compounds in the technical literature of colouring matters. There is, however, no analytical justification for this fallacious formulation, which has been advocated probably owing to two circumstances: first, these lakes are often produced either on the textile fibres or in bulk from ferrous compounds, and, secondly, the deep green colour of the lakes suggests a misleading analogy with the similar although much paler tints of many ferrous salts.

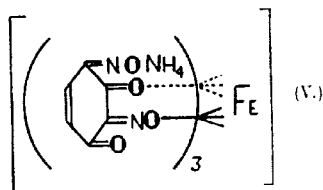
The green quinoneoxime iron lakes can be produced from either ferric or ferrous salts, but in the latter instance lake formation is accompanied by oxidation. The product contains ferric iron in both cases and the intense green colour is characteristic of the heterocyclic complex in which the trivalent iron atom has now become implicated.

When dinitrosoresorcinol and ferrous sulphate interact in presence of ammonia under ordinary atmospheric conditions, a deep green lake is obtained. This product contains no ferrous iron, but has the composition of a basic ferric compound derived from a monochelate mordant dye (IV).



The formation of this basic ferric lake agrees with the analytical data obtained by O. Hoffmann in a study of the iron lakes of 2-nitroso- $\alpha$ -naphthol-4-sulphonic acid (Naphthol Green G), where ferrous salts gave lakes corresponding with a basic ferric constitution (*Ber.*, 1891, **24**, 3741). This investigator noticed that by repeated crystallisation the basic lakes furnished the normal ferric lake, a product which was obtained more directly by the use of a ferric salt.

The interaction of ferric alum and dinitrosoresorcinol in presence of ammonia leads similarly to the normal ferric lake containing one atomic proportion of iron combined with three molecular proportions of the monoammonium salt of the benzodiquinonedioxime radicle (V).



The composition and properties of the cobaltamine and ferric lakes of dinitrosoresorcinol furnish corroborative evidence in support of the view that this dye contains one chelate group and one salt-forming radicle as symbolised in the foregoing constitutional formulæ.

Accordingly, our practical results substantiate the consecutive formula for dinitrosoresorcinol (II) inasmuch as this configuration shows distinctly that the two isonitroso-radicles differ fundamentally in function. The median isonitroso-group alone is involved in the chelating complex, whereas the terminal isonitroso-group situated in the para-position with respect to the remaining carbonyl group

behaves merely as an acidic radicle. A symmetrical formulation (1:2:4:5) for dinitrosoresorcinol suggests on the contrary that both isonitroso-groups have similar functions, thus leading to a dichelate dye. This supposition is entirely opposed to the experimental evidence.

#### EXPERIMENTAL.

Dinitrosoresorcinol was prepared by the method outlined in Cain and Thorpe's "Synthetic Dyestuffs," ed. 1913, page 253, and dried on porous plate over sulphuric acid under reduced pressure. The product then contained one molecule of water (Found: N = 15.08, 15.20.  $C_6H_4O_4N_2 \cdot H_2O$  requires N = 15.04 per cent.) (compare Fitz, *Ber.*, 1875, **8**, 631; Kostanocki, *Ber.*, 1889, **22**, 1345; Bülow and Deighmayr, *Ber.*, 1904, **37**, 1794). A difficulty arose in estimating ammonia in the complex cobalt-ammine lakes of dinitrosoresorcinol owing to the fact that the colouring matter itself evolved ammonia on heating with 5N-sodium hydroxide. The amount set free varied with the time of distillation; in three and a half hours, about one-sixth of the nitrogen present had been eliminated as ammonia and after thirteen and a half hours the proportion of nitrogen eliminated was roughly about one-fourth of the whole; there was no definite end-point. During this distillation, an unmistakably persistent odour of hydrogen cyanide was noticed, and this acid was identified in the distillate as silver cyanide. The exact nature of the decomposition was not ascertained owing to the tarry nature of the non-volatile product.

#### 1-Pentamminocobaltic 3-Cobaltic 1:2:3:4-Benzodiquinone-1:3-dioximate (Formula III).

Dinitrosoresorcinol (5.6 grams) was added to 72 c.c. of 5N-ammonia, diluted with 30 c.c. of water, when a slight brownish-green precipitate was formed, which was dissolved by the further addition of 5 c.c. of 5N-ammonia. This solution of the diammonium salt of dinitrosoresorcinol was mixed with cobaltammine reagent, prepared by adding 2 c.c. of 5N-hydrogen peroxide to 20 c.c. of 2N-cobalt chloride diluted with 40 c.c. of 5N-ammonia. The resulting mixture, containing a chocolate-brown precipitate, was heated at 75° for fifteen minutes and cooled to 0°. The insoluble product, after washing with cold water, was dried over soda-lime in presence of solid ammonium carbonate for three days under 10 mm. pressure [Found: Co = 15.76, 15.83; N = 20.93.  $(C_6H_2O_4N_2 \cdot H_2O)_3 Co_2(NH_3)_5$  requires Co = 15.61; N = 20.38 per cent.].

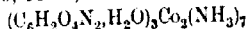
The trihydrate was now dried over quicklime for three days under



10 mm. pressure [Found: Co = 16.33, 16.44;  $\text{NH}_3$  = 11.72, 11.33; N = 22.12; another dehydrated preparation gave Co = 16.95, 16.81; N = 21.31, 21.40.  $(\text{C}_6\text{H}_2\text{O}_4\text{N}_2)_3\text{Co}_2(\text{NH}_3)_3$  requires Co = 16.81;  $\text{NH}_3$  = 12.13; N = 21.95 per cent.].

The anhydrous cobaltammine lake was a chocolate-brown, amorphous powder insoluble in water and the ordinary organic media; it evolved ammonia on heating and was decomposed by warm 5*N*-sodium hydroxide. The co-ordinated ammonia was estimated by distillation during one and three-quarters to two hours with aqueous borax (0.3 to 3 per cent.); the total nitrogen was determined by Kjeldahl's method after preliminary reduction with sodium hydrosulphite; equal weights (0.3 gram) of this reducing agent and the cobaltammine lake were digested at 100° with 6 c.c. of 2*N*-sulphuric acid. The mixture was then heated with 5 to 10 c.c. of concentrated sulphuric acid and a globule of mercury. Owing to the explosive nature of the cobaltammine lake, the metal present was estimated as anhydrous sulphate after a preliminary digestion at 100° with 2*N*-sulphuric acid followed by strong heating with concentrated acid, any separated carbon being oxidised by ammonium nitrate. With cold concentrated hydrochloric, nitric, or sulphuric acid, the anhydrous cobaltammine lake developed a reddish-brown coloration, becoming orange on dilution.

A partly chelated lake was obtained by adding slowly a solution of 5.6 grams of dinitrosoresorcinol in 110 c.c. of 15*N*-ammonia to 20 c.c. of 2*N*-cobaltic chloride, dissolved in 55 c.c. of 5*N*-ammonia and 4 c.c. of hydrogen peroxide. A brown, gelatinous precipitate was formed, and after adding 15 c.c. of 15*N*-ammonia the mixture was heated at 60°. The insoluble product, washed successively with water, alcohol, and ether, was dried for four days over soda-lime under 10 mm. pressure in presence of ammonium carbonate [Found: Co = 15.10, 14.89; N = 21.94, 22.63.



requires Co = 14.90; N = 23.05 per cent.].

#### *Ferric Ammonium Lakes of Dinitrosoresorcinol.*

1. *Basic Ferric Lake*: 1-Ammonium 3-Hydroxoferric 1:2:3:4-Benzodiquinone-1:3-dioximate (Formula IV).

Ferrous ammonium sulphate (7.82 grams), dissolved in the least amount of water, was added to 500 c.c. of water and 30 c.c. of 18*N*-ammonia containing 13 grams of dissolved dinitrosoresorcinol, when an intense green coloration was produced. The solution was concentrated on the water-bath to 350 c.c. and cooled. The precipitated lake, after washing with 5*N*-ammonia, was dried for

four days in a vacuum desiccator over soda-lime [Found : C = 33.07, 33.12; H = 3.45, 3.36; N = 19.05 (Kjeldahl), 19.60 (Dumas); Fe = 12.87, 12.92.  $(C_6H_2O_4N_2 \cdot NH_4)_2Fe \cdot OH$  requires C = 32.74; H = 2.97; N = 19.04; Fe = 12.65 per cent.].

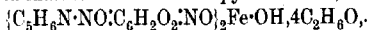
The basic ferric ammonium lake of dinitrosoresorcinol was a black amorphous powder dissolving in water to a dark green solution; its solubility decreased considerably on drying and it dissolved sparingly in alcohol or pyridine; it was insoluble in other organic media, but dissolved readily in aqueous sodium hydroxide or 18*N*-ammonia. With concentrated nitric or sulphuric acid, this lake developed a reddish-brown coloration, becoming orange on dilution. On boiling with concentrated hydrochloric acid to remove dinitrosoresorcinol, the filtrate on dilution gave all the reactions for ferric iron and showed no indication of the ferrous condition. The foregoing results proved conclusively that the lake produced from dinitrosoresorcinol and a ferrous salt in ammoniacal solution exposed to air was entirely a basic ferric compound.

2. *Normal Ferric Lake*: 1-Ammonium 3-Ferric 1:2:3:4-Benzodiquinone-1:3-dioximate (Formula V).

Ferric alum (9.6 grams), dissolved in 100 c.c. of cold water, was added to a solution of 11.2 grams of dinitrosoresorcinol in 450 c.c. of water and 25 c.c. of 15*N*-ammonia. The solution was concentrated in three different experiments to 300, 400, and 500 c.c. of liquid, the yields of green lake being, respectively, 6.9, 8, and 1.4 grams. The precipitates were washed successively with alcohol and ether and dried for five days over concentrated sulphuric acid under 10 mm. pressure [Found: Fe = 9.92, 10.39, 10.44; N = 20.73, 20.11, 20.42.  $(C_6H_2O_4N_2 \cdot NH_4)_3Fe$  requires Fe = 9.17; N = 20.71 per cent.]. These results agree best with the composition of a normal ferric lake. The product is a bluish-black powder soluble in water or pyridine to a dark green solution, but insoluble in neutral ordinary organic media.

Inasmuch as pyridine was one of the few organic solvents in which dinitrosoresorcinol dissolved, an attempt was made to obtain a crystalline ferric pyridine lake. Anhydrous ferric chloride (1.5 grams, 1 mol.), dissolved in 7 grams of pyridine, was added to a solution of 5.35 grams (3 mols.) of dinitrosoresorcinol in 20 grams of the same solvent. Heat was evolved and a dark green coloration developed, but there was no precipitate until 40 c.c. of absolute alcohol were added, when a dark green substance was deposited, which, after washing with alcohol and drying over quicklime in a vacuum desiccator, weighed 3.3 grams. The compound gave a distinct iodoform test for alcohol (Found: C = 48.87; H = 4.44;

N (Dumas) = 11.99, N (Kjeldahl) = 11.41; Fe = 7.62. These analytical data indicate a basic ferric pyridine lake,



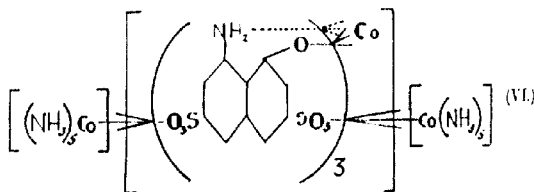
requiring C = 48.18; H = 5.50; N = 11.19; Fe = 7.44; or  $[(C_5H_6N:NO:C_6H_2O_2:NO)_2Fe]_2O \cdot 8C_2H_6O$ , requiring C = 48.75; H = 5.43; N = 11.32; Fe = 7.52 per cent. It was, however, impossible to ascertain precisely by analysis the degree of hydration. This ferric pyridine lake was sparingly soluble in water, alcohol, or ether, but dissolved readily in pyridine to a deep green solution.

#### *Cobaltamine Salts of Colour-producing Intermediates.*

In connexion with an investigation still in progress on synthetic mordant azo-dyes, it became of interest to examine the behaviour of the generators of these colouring matters towards the cobaltamine reagent, especially when it was found that complete chelation of the cobaltic complex took place less readily in the benzene than in the naphthalene series.

8-Amino- $\alpha$ -naphthol-3:6-disulphonic acid (H acid) yields a cobaltamine salt (VI) containing a threefold chelated complex, whereas 2-aminophenol-4-sulphonic acid gives only a partly chelated compound even at 75°, and repeated attempts up to 100° have failed to produce more than twofold chelation (formula VII). The case of anthranilic acid is even more exceptional. The cobaltamine reagent gives an insoluble cobaltous anthranilate, which is also formed more simply with ammoniacal cobalt chloride in the absence of hydrogen peroxide. The determining factor in this reaction is in all probability the sparing solubility of cobaltous anthranilate, this salt being removed from the sphere of action before oxidation can occur. The cobalt atom, which exhibits its lower valency, has also the lower co-ordination number of 4 as in the cobaltous  $\alpha$ -oximinoketones recently described by Ponzio (*Gazzetta*, 1922, 52, i, 285).

3:6-Dipentaminocobaltic 1-Cobaltic 8-Amino-1-oxynaphthalene-3:6-disulphonate (Formula VI).

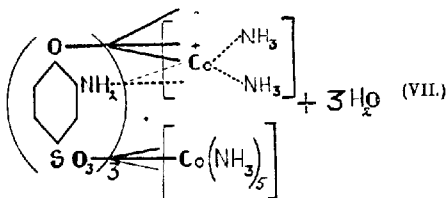


A specially purified specimen of the monosodium salt of H acid, obtained from Dr. de Mouilpied\* of the British Dyestuffs Corpor-

ation, gave Na = 6.08, 6.12; S = 17.91, 17.32 per cent., these numbers corresponding with the acid sodium salt with  $1\frac{1}{2}\text{H}_2\text{O}$  (compare Dressel and Kothe, *Ber.*, 1894, 27, 2137).

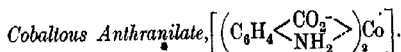
One-third of the cobaltammine reagent from 30 c.c. of 2*N*-cobalt chloride, 45 c.c. of 5*N*-ammonia, and 6 c.c. of 5*N*-hydrogen peroxide was added to a solution of 10.8 grams of this acid sodium salt dissolved in 8 c.c. of 15*N*-ammonia and 10 c.c. of water, and after heating at 100° the mixture was allowed to cool. Following the addition of the remaining two-thirds of cobaltammine reagent, the dark brown, viscid liquid was heated at 60°, the cobaltammine compound being subsequently precipitated by the addition of 150 c.c. of absolute alcohol. The chocolate-brown product after washing with alcohol and ether was dried for a week over soda-lime [Found: Co = 13.45;  $\text{NH}_3$  = 13.60; N = 14.0; S = 13.35.  $(\text{C}_{10}\text{H}_4\text{ONH}_2\cdot\text{S}_2\text{O}_6)_3\text{Co}_3(\text{NH}_3)_{10}$  requires Co = 13.63;  $\text{NH}_3$  = 13.13; N = 14.05; S = 14.84 per cent.]. The cobaltammine compound of H acid dissolved in water to a reddish-brown solution, changing to carmine on adding caustic alkali or to yellow on acidifying. It was insoluble in organic media, evolved ammonia on heating, and developed a heliotrope coloration, changing to carmine, with concentrated sulphuric acid.

*Cobaltammine Salt of 2-Aminophenol-4-sulphonic Acid,*



A solution of 11.5 grams of 2-aminophenol-4-sulphonic acid in 20 c.c. of 15*N*-ammonia and 50 c.c. of water was added to sufficient cobaltammine reagent (see preceding preparation) to furnish sufficient cobalt for a dicobaltic salt. The purplish-brown liquid was heated at 60°, cooled, treated with 30 c.c. of alcohol, filtered, and diluted with 250 c.c. of alcohol. The brown precipitate after washing with alcohol and ether was dried for a week over soda-lime under 10 mm. pressure: found Co = 13.75;  $\text{NH}_3$  = 13.66. This preparation, redissolved in dilute ammonia and heated again at 60°, gave, after similar treatment, Co = 13.52;  $\text{NH}_3$  = 14.00. Another specimen, after heating at 75°, gave Co = 14.54;  $\text{NH}_3$  = 13.62. These analyses give the ratio, Co atoms: $\text{NH}_3$  molecules = 2:7, corresponding with the 'partially chelated compound

$(C_6H_3ONH_2 \cdot SO_3 \cdot H_2O)_3Co_2(NH_3)_7$ , which requires  $Co = 13.82$ ;  $NH_3 = 13.96$  per cent.



To 8.2 grams of anthranilic acid (3 mols.), dissolved in 15 c.c. of 5*N*-ammonia, was added the following cobaltammine reagent (1 mol.): 20 c.c. of 2*N*-cobaltous chloride, 22 c.c. of 10*N*-ammonia, and 4 c.c. of 6*N*-hydrogen peroxide. On warming at 80°, the solution yielded a dark brown precipitate which assumed a light grey colour after washing with alcohol and ether [Found:  $Co = 17.45$ ;  $N = 9.40$ .  $(C_7H_6O_2N)_2Co$  requires  $Co = 17.77$ ;  $N = 8.45$  per cent.]. The product contained 1.62 per cent. of ammonia. The preparation was repeated with two molecular proportions of anthranilic acid; the grey product contained  $Co = 17.47$ ;  $N = 8.70$ ; and only 0.83 per cent. of ammonia.

These results showed that the foregoing product was essentially cobaltous anthranilate, and not a cobaltammine salt. The preparation was now modified by using ammoniacal cobaltous chloride (1 mol.) to two molecular proportions of anthranilic acid but no hydrogen peroxide. The cobaltous anthranilate, an amorphous, grey powder insoluble in water and the ordinary organic media, gave  $Co = 17.60$ ;  $N = 9.10$ ; and only 0.68 per cent. of ammonia. Anthranilic acid, melting at 141°, was set free either by hydrochloric acid or on prolonged digestion with boiling water.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expenses of this investigation.

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#### CCCXLIV.—*Researches on Residual Affinity and Co-ordination. Part XIII. Cobaltammine and Chromic Lakes of the Azo-salicylic Acids.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN our earlier communications on mordant dyes (T., 1921, 119, 704; this vol., p. 160), we have shown that the quinoneoxime and alizarin colouring matters, when treated with hydroxopentamminocobaltic chloride ("cobaltammine reagent," this vol., p. 1969),

furnish cobaltic lakes in which at least one radicle of the colour molecule is capable of acting as a chelate group in satisfying the whole of the chemical affinity of trivalent cobalt, so that this implicated metallic atom no longer retains the property of co-ordinating with ammonia. Any ordinary salt-forming group present in the dye such as the hydroxyl, carboxyl, or sulphonyl radicle, loses hydrogen in exchange for the pentamminocobaltic group,  $\text{Co}(\text{NH}_3)_5$ . Hence the cobalt and ammonia content of the cobaltamine lakes of quinonoxime dyes and of the monochelate dyes of the alizarin series can be expressed by the simple numerical relation  $m = 5(n - 1)$ , where  $m$  and  $n$  represent, respectively, the numbers of ammonia molecules and cobalt atoms.

It has since been shown that chelate groups do not occur in the substantive nitro-dyes (picric acid, aurantia, dinitro- $\alpha$ -naphthol and its sulphonic acid, this vol., p. 1723), so that presumably these chelate groups are characteristic of acidic mordant dyes.

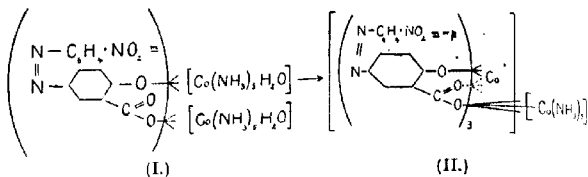
The cobaltamine reagent has also been applied to the case of dinitrosoresorcinol (this vol., p. 2857) with the result that this colouring matter, despite its two nitroso- or isonitroso-groups, was proved to be a monochelate dye, thus falling into line with the nitrosonaphthols.

The method, being thus shown to be of general application, has now been extended to the azosalicylic acids, a group of colouring matters which, although substantive for wool, are generally applied in conjunction with chrome mordants.

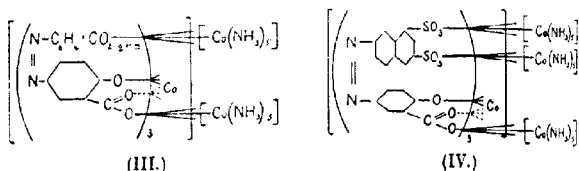
On treating *m*-nitrobenzenesazosalicylic acid and its congeners with the cobaltamine reagent at  $70^\circ$ , cobaltamine lakes are produced which demonstrate the existence of a chelate group analogous to that present in alizarin. The hydroxyl and contiguous carbonyl radicles of the salicylate residue form the chelate group. The other hydroxyl group attached to the carboxylic carbon atom acts as a salt-forming group, its hydrogen becoming replaced by one principal valency of the pentamminocobaltic radicle (Fig. 2). Six mordant dyes of this series have been examined, five being derived from salicylic acid and one from 2:3-hydroxynaphthoic acid (m. p.  $216^\circ$ ).

*m*-Nitrobenzenesazosalicylic acid (Alizarin Yellow GG) and *p*-nitrobenzenesazosalicylic acid (Alizarin Yellow R) reacted with cobaltamine reagent, giving pentamminocobaltic lakes, both represented by formula II. The foregoing lake formation was also effected in two stages, using *m*-nitrobenzenesazosalicylic acid as the example. At the ordinary temperature, this acid reacts with aquo-pentamminocobaltic hydroxide,  $[\text{H}_2\text{O}, \text{Co}5\text{NH}_3](\text{OH})_3$ , yielding the complex diroseo-salt (formula I). This compound is, however,

unstable in boiling water or hot aqueous ammonia and decomposes, with loss of half its ammonia, into the chelated lake (formula II), the change being irreversible.



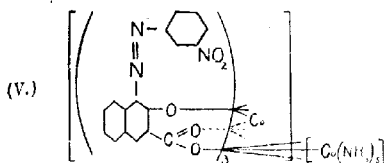
*o*-Carboxybenzeneazosalicylic acid (Diamond Yellow R) and *m*-carboxybenzeneazosalicylic acid (Diamond Yellow G) reacted with a larger proportion of cobaltamine reagent, inasmuch as each of these colouring matters contains an extra salt-forming carboxyl group. The resulting complex lakes each contain three cobalt atoms and ten molecular proportions of ammonia as indicated in graphic formula III.



A still more complex lake is produced by the use of 6:8-disulpho-naphthalene-3-azosalicylic acid (Crumpsall Yellow), and since this colouring matter carries three salt-forming groups the product contains four cobalt atoms and fifteen molecular proportions of ammonia as shown in formula IV.

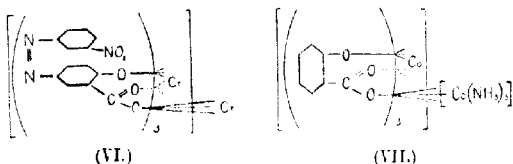
The replacement of salicylic acid by 2-hydroxy-3-naphthoic acid leads to experimental difficulties owing to the circumstance that the dyes produced from this naphthalene intermediate are much more prone to oxidation under the influence of the cobaltamine reagent than is the case with the simpler azosalicylic acid dyes studied in this investigation. This difficulty is, moreover, a significant one, as it suggests that the cobaltamine method may break down when applied to oxidisable dyes. Nevertheless, in spite of the oxidising action of the reagent, it is possible to obtain evidence of the formation from *m*-nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid of a dicobaltic lake containing the normal proportions of cobalt and ammonia ( $\text{Co} : \text{NH}_3 = 2 : 5$ ). Besides containing an oxidisable naphthalene residue, this lake differs in another important respect from the foregoing members of the series under

examination. Its azo-radicle is in the ortho-position to the chelate group, the constitution of the complex lake being represented by formula V, whereas in the azosalicylates these substituents are mutually in the para-position.



A survey of the foregoing diagrams shows that although these cobaltammine lakes of hydroxyazo-dyes derived from salicylic acid and 2:3-hydroxynaphthoic acid vary in complexity with the number of salt-forming groups, yet they all conform to the general type now identified as characteristic of monochelate dyes, the relationship of ammonia molecules ( $m$ ) to cobalt atoms ( $n$ ) as expressed in the equation  $m = 5(n - 1)$ , which has now been found to hold for three series of mordant dyes, the quinoneoxime group, the azosalicylates, and the monochelate dyes of the alizarin series.

That the cobaltammine lakes of the azosalicylic acid dyes have a definite relationship to the chromic lakes of these colouring matters is shown by preparing the yellowish-buff chromic lake from sodium *m*-nitrobenzeneazosalicylate and chrome alum. This simple



lake (VI) contains two atomic proportions of chromium to three molecular proportions of the azosalicylate-radicle, thus conforming to the general type exhibited by the complex cobaltammine lakes. Moreover, salicylic acid itself contains the chelate group which is operative in the foregoing lakes, and should accordingly furnish a cobaltammine lake of similar type. This anticipation has been realised experimentally by the isolation of the sage-green salicylic lake (VII) as a by-product in the preparation of the salicylato-cobaltammines (this vol., p. 1956). The salicylato-radicle, therefore, is a noteworthy instance of a chelate group which can function in two different ways; one of its isomeric forms giving rise to the soluble crystallisable salicylato-cobaltammines, the other yielding the insoluble salicylic lake.



## EXPERIMENTAL.

*Pentamminocobaltic m-Nitrobenzeneazosalicylate* (Formula II).

One-hundredth of a gram-molecule (8.61 grams) of *m*-nitrobenzeneazosalicylic acid (synonyms Alizarine Yellow GG [M] and Chrome Yellow R [P]) was dissolved by boiling in 20 c.c. of 10*N*-ammonia and 30 c.c. of water; the deep red solution treated with 64 c.c. of cobaltammine reagent (1.18 grams Co), a thick brown precipitate was formed and the mixture after warming at 60° for half an hour was cooled on ice. The yield of dark buff cobaltammine lake after washing with dilute ammonia and water and drying over soda-lime was quantitative [Found: Co = 11.1; NH<sub>3</sub> = 8.0; N = 18.4. (C<sub>13</sub>H<sub>7</sub>O<sub>5</sub>N<sub>3</sub>)<sub>3</sub>Co<sub>2</sub>(NH<sub>3</sub>)<sub>5</sub> requires Co = 11.2; NH<sub>3</sub> = 8.0; N = 18.5 per cent.]. This lake was also obtained in a yield of 93 per cent., calculated on the dye, when a 50 per cent. excess of cobaltammine reagent was employed. It was insoluble in water, dilute acids, strong ammonia, pyridine, or organic solvents; it dissolved sparingly in 5*N*-sodium hydroxide with yellow to red colorations and evolving ammonia on boiling. In methyl sulphate, and in all concentrated acids, it developed intense red colorations distinct from those of the free azo-dye, the latter being precipitated on dilution.

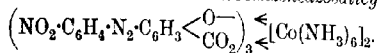
*Bis-aquopentamminocobaltic m-Nitrobenzeneazosalicylate* (Formula I).

Aquopentamminocobaltic chloride (5.4 grams in 20 c.c. of water) was triturated with excess of silver oxide and the filtrate containing aquopentamminocobaltic hydroxide (roseo-base) thoroughly stirred with 5.74 grams of alizarin yellow GG, when an intense brown solution was formed, from which a brown precipitate separated immediately. The trituration was continued for three hours, no ammonia being evolved; the precipitate was then washed successively with water, alcohol, and ether and dried over calcium chloride; the yield was quantitative: Found: Co = 10.3; NH<sub>3</sub> = 14.3. (C<sub>13</sub>H<sub>7</sub>O<sub>5</sub>N<sub>3</sub>)<sub>3</sub>[Co(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sub>2</sub> requires Co = 10.0; NH<sub>3</sub> = 14.4 per cent. This bis-aquopentammine salt was readily soluble in cold 5*N*-sodium hydroxide to an intense orange-yellow solution, but was only sparingly so in 5*N*-ammonia. Methyl sulphate or concentrated sulphuric acid developed intense yellow colorations resembling those obtained from the dye and differing from the red colour produced with the chelated lake.

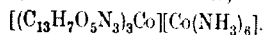
On boiling with water, 1 gram of the aquopentammine salt lost half its ammonia quantitatively within fifteen minutes, passing into the foregoing chelated lake, the latter compound then undergoing a very slow decomposition amounting to the elimination of less than one molecular proportion of ammonia in an hour. The

experiment suggested that the chelated lake, although appreciably unstable in boiling water, would exist unchanged at this temperature in the presence of ammonia. This anticipation was verified by boiling for two hours 1.5 grams of the aquopentammine (roseo-salt) with 100 c.c. of 5*N*-ammonia, the ammoniacal content of the solution being maintained by the occasional addition of drops of 18*N*-ammonia. The reddish-brown aquopentammine assumed a yellowish-buff colour, the product (98 per cent. yield), which was insoluble in cold 5*N*-sodium hydroxide, developed intense red colorations with methyl sulphate or concentrated sulphuric acid, being thus identified as pentamminocobaltic *m*-nitrobenzeneazosalicylate (II) (Found: Co = 11.2; NH<sub>3</sub> = 8.0 per cent.).

*Bis*hexamminocobaltic *m*-Nitrobenzeneazosalicylate,



Alizarin Yellow GG was triturated for three hours with a solution of hexamminocobaltic hydroxide (luteo-base); the product was extracted with cold pyridine to remove unchanged dye, washed with ether, and dried at the ordinary temperature over sulphuric acid: Found: Co = 9.3; NH<sub>3</sub> (evolved in boiling water) = 7.8; total NH<sub>3</sub> = 15.7. (C<sub>13</sub>H<sub>7</sub>O<sub>5</sub>N<sub>3</sub>)<sub>3</sub>[Co(NH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>·5H<sub>2</sub>O requires Co = 9.3; 3NH<sub>3</sub> = 8.1; 12NH<sub>3</sub> = 16.1 per cent. The product after boiling with water was a buff yellow lake developing orange-yellow colorations with methyl sulphate or strong sulphuric acid; a chelated lake, it differed from the others under examination in belonging, not to the purpureo-, but to the luteo-series,



*Pentamminodibaltic p*-Nitrobenzeneazosalicylate (Formula II).

A warm solution of 8.61 grams of *p*-nitrobenzeneazosalicylic acid (synonyms Alizarin Yellow R [*M. By. C.R.*], Terracotta [G], Chrome Orange [P]) in 12 c.c. of 15*N*-ammonia and 60 c.c. of water was added to 45 c.c. of cobaltamine reagent (Co = 1.18 grams) and 20 c.c. of water. The mixture, containing a thin, reddish-chocolate paste, was warmed at 70° and then cooled. The insoluble lake (yield quantitative) was washed successively with dilute ammonia, water, alcohol, and ether and dried over soda-lime [Found: Co = 10.9; NH<sub>3</sub> = 8.2; N = 17.5. (C<sub>13</sub>H<sub>7</sub>O<sub>5</sub>N<sub>3</sub>)<sub>2</sub>(Co<sub>2</sub>(NH<sub>3</sub>)<sub>5</sub>) requires Co = 11.2; NH<sub>3</sub> = 8.0; N = 18.5 per cent.]. The lake, which slowly evolved ammonia on keeping, was insoluble in pyridine and other organic solvents, except methyl sulphate, with which it developed an intense red coloration similar to that obtained with strong acids. With hot 5*N*-sodium hydroxide, it evolved ammonia and dissolved to a red solution.

*3:3'-Dipentammino-3:4:3'-tricobaltic Benzene-1-azo-4-oxycarboxy-  
3:3'-dicarboxylate* (Formula III).

The deep red solution containing one-hundredth of a gram molecule of *m*-carboxybenzeneazosalicylic acid (Diamond Yellow G [By]), dissolved by boiling with 12 c.c. of 15*N*-ammonia and 30 c.c. of water, was added to 60 c.c. of cobaltamine reagent (Co = 1.77 grams) and the mixture warmed at 70°. A buff precipitate separated which on analysis proved to be a mixture of the lake and ammonium salt of the azo-compound. Accordingly, the product was treated twice in succession with molecular proportion of cobaltamine reagent. The final residue, a khaki-brown powder (yield 30 per cent.) gave the following data: Co = 14.8; NH<sub>3</sub> = 14.4; N = 18.2. [(C<sub>14</sub>H<sub>7</sub>O<sub>5</sub>N<sub>2</sub>)<sub>3</sub>Co]<sub>2</sub>[Co(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub> requires Co = 14.8; NH<sub>3</sub> = 14.2; N = 18.7 per cent. This tricobaltic lake, which slowly evolved ammonia on keeping, was slightly soluble in water or cold dilute aqueous alkalis to yellow solutions; with hot 5*N* sodium hydroxide it evolved ammonia and dissolved with an orange colour. Insoluble in concentrated aqueous ammonia, pyridine, and organic media excepting methyl sulphate, it dissolved in the last solvent to an intense red solution similar to that obtained with concentrated acids.

*2:3'-Dipentammino-2':3:4-tricobaltic Benzeneazo-4-oxycarboxy-  
2':3-dicarboxylate* (Formula III).

The warm reddish-orange solution of one-hundredth of a gram molecule of *o*-carboxybenzeneazosalicylic acid (Diamond Yellow R [By]) in 6 c.c. of 15*N*-ammonia and 20 c.c. of boiling water was added to 100 c.c. of cobaltamine reagent (Co = 1.77 grams). A slight buff precipitate appeared, but redissolved on warming at 70° and no further separation was effected on cooling until 5 volumes of alcohol were added, when a reddish-brown lake was precipitated, which was washed successively with dilute alcohol, alcohol, and ether (yield 70 per cent.): Found: Co = 14.6; NH<sub>3</sub> = 14.1; N = 18.4. [(C<sub>14</sub>H<sub>7</sub>O<sub>5</sub>N<sub>2</sub>)<sub>2</sub>Co]<sub>2</sub>[Co(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub> requires Co = 14.8; NH<sub>3</sub> = 14.2; N = 18.7 per cent. The colour reactions are similar to those of the preceding lake.

*3':6:8-Tripentammino-3':4':6:8-tetracobaltic 6:8-Disulphonaphthalene-2-azo-4'-oxycarboxybenzene-3'-carboxylate* (Formula IV).

The warm intensely red solution of 7.11 grams (one two-hundredth of a molecule) of the acid sodium salt of 6:8-disulphonaphthalene-β-azosalicylic acid (Crumpsall Yellow [Lev.]) obtained by dissolving the dye in boiling water (10 c.c.) and 12 c.c. of 5*N*-ammonia,

was added to 56 c.c. of cobaltammine reagent (Co = 1.77 grams or 50 per cent. excess). A viscid, dark brown precipitate appeared and redissolved on warming at 70°. On cooling the intensely red solution to 0°, a microcrystalline precipitate separated (yield 54 per cent.) and was washed successively with dilute ammonia, water, alcohol, and ether and dried over calcium chloride and soda-lime: Found: Co = 13.5;  $\text{NH}_3$  = 14.4; N = 15.7; S = 9.1.  $[(\text{C}_{17}\text{H}_8\text{O}_9\text{N}_2\text{S}_2)_3\text{Co}]\{\text{Co}(\text{NH}_3)_5\}_3$  requires Co = 12.9;  $\text{NH}_3$  = 13.9; N = 16.0; S = 10.5 per cent. This crystalline lake, which dissolved in water or dilute caustic alkalis to a brownish-yellow or reddish-orange solution, respectively, evolved ammonia with hot aqueous alkali; it was soluble in dilute acids to a reddish-purple solution, concentrated acids and methyl sulphate giving a carmine-red coloration and becoming purple and orange on dilution. Insoluble in pyridine, it dissolved sparingly in concentrated ammonia.

*Dichromic m-Nitrobenzeneazosalicylate* (Formula VI).

*m*-Nitrobenzeneazosalicylic acid (8.6 grams), dissolved to a deep red solution by boiling in 30 c.c. of *N*-sodium hydroxide and 50 c.c. of water, was added to 65 c.c. of 0.46*N*-chrome alum (= 0.52 gram Cr), when a lemon-yellow precipitate appeared, assuming a buff colour on boiling. This product, extracted with benzene in a Soxhlet apparatus, yielded 1.5 grams of dye insoluble in this solvent [Found: Cr = 10.6; N = 12.7.  $(\text{C}_{13}\text{H}_7\text{O}_5\text{N}_3)_2\text{Cr}_2$  requires Cr = 10.8; N = 13.1 per cent.].

This dichromic lake was insoluble in organic media, in water, and in cold dilute acids and alkalis. It dissolved to a yellow solution in hot 5*N*-sodium or ammonium hydroxide, in pyridine to a yellow solution, in methyl sulphate to a red solution, and in concentrated nitric or sulphuric acid to an orange solution. It was insoluble in, but changed to brick-red by, concentrated hydrochloric or syrupy phosphoric acid.

*3-Pentammino-2:3-dicobaltic m-Nitrobenzene-1-azo-2-oxo-3-naphthoate* (Formula V).

*m*-Nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid was prepared by coupling *m*-nitrobenzenediazonium chloride (6.9 grams  $\text{NO}_2\text{C}_6\text{H}_4\text{NH}_2$ ) with 2:3-hydroxynaphthoic acid (9.9 grams) in 80 c.c. of 5*N*-sodium hydroxide and 200 c.c. of *N*/2-sodium acetate; the solution, containing a deep red deposit, was warmed at 80° and acidified; the vermilion precipitate, when crystallised from pyridine, in which it was moderately soluble, separated in coppery-red needles melting at 271–273° (Found: N = 13.0.  $\text{C}_{17}\text{H}_{11}\text{O}_5\text{N}_3$  requires N = 12.5 per cent.). This azo-pigment was insoluble in

water or concentrated hydrochloric acid and dissolved only sparingly in aqueous ammonia or caustic alkalis. Methyl sulphate and concentrated sulphuric acid developed intense carmine-red colorations.

When 7.4 grams of the azo-hydroxynaphthoic acid were suspended in 60 c.c. of hot 5*N*-ammonia and treated with 48 c.c. of cobaltammine reagent, a brownish-red product separated which assumed a chocolate colour on heating the mixture to 60°. After cooling over-night, the supernatant liquid and a small amount of oxidised scum were decanted; the residue was washed successively with dilute ammonia, water, and alcohol, 8.4 grams of the brown lake being obtained [Found: Co = 10.3; NH<sub>3</sub> = 8.9. (C<sub>17</sub>H<sub>9</sub>O<sub>5</sub>N<sub>3</sub>)<sub>3</sub>Co(NH<sub>3</sub>)<sub>5</sub> requires Co = 9.8; NH<sub>3</sub> = 7.0 per cent.]. It was insoluble in water, aqueous alkalis, and dilute acids; it dissolved in pyridine to an intense brown solution and developed deep red colorations with methyl sulphate and concentrated nitric acid or sulphuric acid.

*Pentammino-1 : 2-dicobaltic 2-Oxybenzoate (Pentamminodicobaltic Trisalicylate) (Formula VII).*

Reference has already been made (this vol., p. 1961) to the formation of the cobaltammine lake of salicylic acid as a by-product in the preparation of salicylatocobaltammine salts, the maximum yield being about 12 per cent. It was thus obtained as a sage green powder insoluble in water, dilute acids or alkalis, and the ordinary organic solvents including pyridine [Found: Co = 17.7; NH<sub>3</sub> = 12.7. (C<sub>7</sub>H<sub>4</sub>O<sub>3</sub>)<sub>3</sub>Co<sub>2</sub>(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>3</sub> requires Co = 17.7; NH<sub>3</sub> = 12.8 per cent.]. This lake, which was also obtained from disodium salicylate and a boiling solution of hexamminocobaltic chloride, evolved ammonia on warming with 5*N*-sodium hydroxide; it developed brown colorations with methyl sulphate and concentrated sulphuric or nitric acid. Hot concentrated hydrochloric acid decomposed it with evolution of chlorine into salicylic acid and a green solution of cobaltous chloride.

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CCCXLV.—*Boundary Lubrication and Chemical Constitution. The Optically Active Carbinols of the Formula  $C_2H_5\cdot CH(OH)\cdot C_nH_{2n+1}$ .*

By IDA DOUBLEDAY.

IN measurements of lubricating power, a slider having a spherical face is applied to a plane surface, lubricated with the substance under investigation, in an atmosphere of perfectly clean, dry air. The conditions operating are those of "boundary lubrication," and the horizontal force which just fails to cause motion of the slider immediately it is applied is taken as a measure of the static friction.

It has already been shown (Hardy and Doubleday, *Proc. Roy. Soc.*, 1921, [A], 100, 550) that for certain homologous series of carbon compounds, the coefficient of static friction ( $\mu$  = pull in grams divided by weight of slider) is a linear function of the molecular weight of the lubricant. With the exception of the lowest two members of the acid series, formic and acetic acids, this relation holds strictly for the normal paraffins and their related primary alcohols and acids.

Through the kindness of Dr. Pickard, the author has now had the opportunity of examining a long homologous series, comprising the optically active forms of fourteen normal secondary alcohols of the formula  $C_2H_5\cdot CH(OH)\cdot C_nH_{2n+1}$  (where  $n$  varies from 1 to 15) prepared by himself and Dr. Kenyon (T., 1913, 105, 1923). These carbinols are of extreme purity. In the homogeneous state, abnormality as regards molecular rotatory power was found when  $n = 5$  (or 6), 10 (or 11), or 15 (*loc. cit.*); that is, at those members of the series where the growing chain may be expected, from stereochemical considerations, all but to return on itself. The viscosities of the members of two similar series,  $CH_3\cdot CH(OH)\cdot C_nH_{2n+1}$  and  $(CH_3)_2CH\cdot CH(OH)\cdot C_nH_{2n+1}$ , and the esters of these, were determined by Dunstan and Thole (T., 1913, 103, 127; 1914, 105, 782), but no similar abnormalities were observed, and the curves connecting the logarithms of viscosity with molecular weights in each series were found to be linear.

It was suggested by Dr. Pickard that lubricating power might be a more highly constitutive property than viscosity, and that measurements of  $\mu$  might give some indication of the spiral form of the growing carbon chain; the present investigation was therefore undertaken with the object of testing this suggestion.

#### EXPERIMENTAL.

The apparatus and experimental method have been fully described in earlier papers (Hardy, *Phil. Mag.*, 1919, [vi], 39, 32; Hardy and

Doubleday, *Proc. Roy. Soc.*, 1921, [A], **100**, 550; 1922, [A], **101**, 487).

Measurements were made on glass and steel and with the lubricants both in the flooded state and as a primary film formed by spreading. The solid carbinols (ethyl-*n*-octylcarbinol and all higher members) were deposited as invisible films from pure, dry ether, and were also used in the liquid state, the temperature in the experimental chamber being regulated to about 1° above the melting point of the solid; previous investigation having shown that, at any rate from 15° to 110°,  $\mu$  is independent of the temperature so long as the lubricant is completely fluid or is applied as an invisible film. The possibility of partial racemisation with increase of temperature could be disregarded, as these optically active carbinols are known to be extremely stable.

The values of the coefficient of friction,  $\mu$ , are given below for flooding and primary films on glass and steel (Table I). It will be seen that within the limits of experimental error the corresponding flooded and film values are identical in each case.

TABLE I.

Lubricant.	Lubricants on Glass.		Lubricants on Steel.	
	Flooded.	Primary film.	Flooded.	Primary film.
<i>d</i> -Methylethylcarbinol .....	0.6215	0.6246	0.4453	0.4416
Diethylcarbinol .....	0.5206	0.5192	0.3501	0.3552
<i>d</i> -Ethyl- <i>n</i> -propylcarbinol ....	0.4657	0.4623	0.2962	0.2973
<i>d</i> -Ethyl- <i>n</i> -butylcarbinol .....	0.4400	0.4454	0.2680	0.2643
<i>d</i> -Ethyl- <i>n</i> -amylcarbinol .....	0.4105	0.4098	0.2378	0.2378
<i>d</i> -Ethyl- <i>n</i> -hexylcarbinol .....	0.3812	0.3812	0.2152	0.2206
<i>dl</i> -Ethyl- <i>n</i> -hexylcarbinol .....	0.3124	0.3087	0.1563	0.1507
<i>d</i> -Ethyl- <i>n</i> -heptylcarbinol ....	0.3531	0.3495	0.1834	0.1804
<i>d</i> -Ethyl- <i>n</i> -octylcarbinol .....	0.3282	0.3304	0.1605	0.1577
<i>d</i> -Ethyl- <i>n</i> -nonylcarbinol .....	0.3006	0.2986	0.1298	0.1309
<i>l</i> -Ethyl- <i>n</i> -decylcarbinol .....	0.2713	0.2701	0.1072	0.1054
<i>l</i> -Ethyl- <i>n</i> -undecylcarbinol ....	0.2423	0.2377	0.0701	0.0684
<i>l</i> -Ethyl- <i>n</i> -dodecylcarbinol ....	0.3814	0.3829	0.2024	0.2001
<i>l</i> -Ethyl- <i>n</i> -tridecylcarbinol ....	0.1904	0.1868	0.0226	0.0218
<i>l</i> -Ethyl- <i>n</i> -pentadecylcarbinol	0.1351	0.1364	unmeasurable; slider moves with weight of scale pan.	unmeasurable; slider moves with weight of scale pan.

If these values of  $\mu$  are plotted against molecular weights, the curves shown in Fig. 1 are obtained, the upper curve being for glass, the lower for steel.

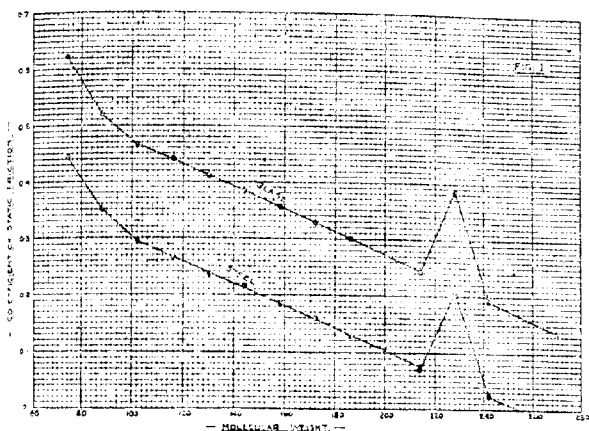
#### Discussion of Results.

It will be seen that, except in the case of the methyl, ethyl, and dodecyl carbinols, the values of  $\mu$ , when plotted against molecular weight, lie on a straight line, and moreover, the curves for glass and

steel are parallel. The slope of the curves is slightly greater than that of the normal primary alcohol series, given in a previous paper (*loc. cit.*). Therefore, if the first two and the twelfth members of the series be neglected, the curves satisfy the equation

$$\mu = b - aM$$

where  $M$  is molecular weight of the lubricant;  $a$  is a parameter independent of the nature of the solid face and dependent only on chemical type, varying from one chemical series to another; and  $b$  is dependent on the nature of the solid face, as well as on the chemical series. This is the relation previously shown to obtain for normal paraffins, alcohols, and acids (see earlier papers).



Any abnormalities due to the spiral arrangement of the carbon chain should be shown when either the branch chain or the whole chain of the carbinol molecule contains a multiple of five carbon atoms. That is, departure from linearity might be expected at the amyl, decyl, and pentadecyl carbinols (5, 10, and 15 carbon atoms in the branch chain); or at the ethyl, heptyl, and dodecyl carbinols (5, 10, and 15 carbon atoms in the whole chain). Actually abnormality is found in two cases where the number of carbon atoms in the whole chain equals a multiple of five, that is, at the ethyl and dodecyl members. A glance at the curves, however, will show that some explanation other than the disposition of carbon atoms in the chain will have to be found to account for the abnormality, for no trace of irregularity is shown by the heptyl member, and further, it is highly improbable that the effect for a chain of fifteen



carbon atoms would be greater than for one of five, yet the actual abnormality shown by the dodecyl carbinol is very much greater than that of the diethyl compound. It is evident, therefore, that the spiral arrangement of the carbon chain, if it exists, exerts no influence on the lubricating power. This is in agreement with the view, advanced by Hardy, that in the primary films with which we are dealing in lubrication measurements, "the atomic pattern of the molecules suffers rearrangement, somewhat like that which occurs in crystal formation. The primary film in a sense may be said to be crystallised" (*Proc. Roy. Soc.*, 1921, [A], **100**, 570).

In the case of the dodecyl carbinol, the abnormally high value of  $\mu$  is hard to explain, unless we assume that the sample was contaminated by some impurity. It is known that a minute percentage of impurity may affect the lubricating power enormously; thus, the merest trace of moisture will raise the value of  $\mu$  for the primary alcohols nearly to the "clean" value ( $= 0.94$  for the glass used). The compounds employed in the present investigation were, as has already been stated, of an extremely high degree of purity, strong confirmation for this being found in the general linearity of the curves. It is possible, nevertheless, that a trace of moisture or other foreign substance had found its way into the specimen of dodecyl carbinol, and that the exaltation of friction was due to this. There seems to be no other possible explanation. It may be noted that this carbinol has also been found to be slightly abnormal as regards density.

The departure from linearity shown by the methyl and ethyl carbinols is not unexpected, since with almost every physical property, the results for the first one or two members of an homologous series tend to anomaly. This is often ascribed, in the case of hydroxyl compounds, to the high degree of association possessed by the initial members. In the case here considered, however, the abnormality is in the wrong direction. Association, by increasing the molecular weight, would tend to lower the value of  $\mu$ , whereas actually the values obtained for the two compounds are higher than would be expected. An associated molecule would have less residual affinity than a single molecule, therefore it is possible that if association does occur, the diminished friction due to increased molecular weight is more than balanced by the increase due to diminished residual affinity.

There remains one more point of interest to be noted. Of the active compounds examined, some were dextro- and some laevo-rotatory, and from the results obtained it is evident that the lubricating power is independent of the sign of rotation. It was found, however, that the *dl*-modification of ethylhexylcarbinol

gave a value for  $\mu$  considerably lower than that of the corresponding *d*-carbinol (see Table I). Several measurements were made, but the same low value was always obtained. At present, no other *dl*-compound has been examined, but if this result was not due to impurity and can be confirmed in other cases, it is of considerable theoretical importance as indicating that the molecular conditions of the inactive and active liquids are different.

The question of the existence of liquid racemates is one over which there has been a great deal of controversy, and the evidence obtained has been conflicting. Various physical properties of liquids have been utilised in an attack on the problem, such as the molecular volume, viscosity values (Thole, T., 1913, 103, 19), absorption power (Steward, T., 1907, 91, 1537), refractive index (Pope and Peachey, T., 1899, 75, 1111), and molecular weight as determined by Ramsay and Shields's surface tension method (Mitchell and Smith, T., 1913, 103, 489). In spite of the huge accumulation of data, none of the methods employed can be said to have definitely established the existence of liquid racemates, and in the case of the normal secondary alcohols the methods hitherto used have given negative results only. The application of lubrication measurements should be eminently suitable for investigating this problem, since the lubricating power of a liquid is very essentially a molecular function. It is, of course, impossible to theorise on the single example given above, but it is hoped to continue the investigation by examining several *dl*-liquids and their corresponding dextro- and levo-rotatory forms.

In conclusion, the author wishes to express her best thanks to Dr. Pickard for suggesting the research and for the loan of material.

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## CCCLXVI.—Vat Dyes of the Azo-series.

By DHIRENDRA NATH MUKERJI.

THIS work was undertaken with the object of discovering a method by which insoluble azo-dyes could be fixed on textile fibres.

The investigation of Green and Bearder (T., 1911, 99, 1960) on nitrohydrazo-compounds suggested the idea that suitable nitroazo-compounds might be applied as vat dyes. It was found that *pp'*-dinitrohydrazobenzene was absorbed by wool from dilute alkaline solution and on exposing the fibres to air the corresponding

dinitroazobenzene was regenerated within the fibres, but the dyeings were not so fast to washing and alkalis as expected. The preparation of similar compounds of deeper colour was then attempted, and three azo-dyes were prepared. Of these, *p*-nitrobenzeneazo-4-nitro- $\alpha$ -naphthol and *p*-nitrobenzeneazo-*o*-nitrophenol could be reduced to the corresponding hydrazo-compounds with alcoholic ammonium sulphide. The reduction of the third compound, 4-nitronaphthaleneazo-4-nitro- $\alpha$ -naphthol, could not be tried on account of its small yield. The hydrazo-compounds thus obtained were not very soluble in dilute aqueous alkali. However, it was found possible to use them as vat dyes and to regenerate the azo-compounds by exposing the fibres to air. But the method does not seem to be very promising, as the dyeings have not the desired fastness. Moreover, the hydrazo-compounds are not readily soluble in very dilute aqueous alkali, which alone is suitable for a wool-dyeing bath. Cotton, which will withstand more concentrated alkali, does not readily absorb the hydrazo-compounds.

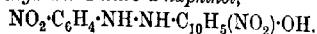
#### EXPERIMENTAL.

*pp'*-Dinitrohydrazobenzene.—This compound was prepared according to Green and Bearder (*loc. cit.*).

*Wool Dyeing*.—0.05 Gram of the substance was dissolved by boiling with 15 c.c. of water containing 0.06 gram of potassium hydroxide (six times the theoretical amount). One gram of wool was then introduced into the vat, which was kept at the laboratory temperature. The wool was taken out after an hour, well wrung, and exposed to the air for two to three hours. The colour of the dyeing changed from deep blue to golden-yellow.

*Cotton Dyeing*.—Cotton was dipped in a 6 per cent. aqueous potash solution of the dyestuff (5 per cent. by weight of the cotton used). The colour changed from light blue to yellow by oxidation in air. It was found that very little of the dyestuff was taken up by cotton.

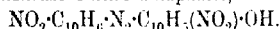
*p*-Nitrobenzeneazo-4-nitro- $\alpha$ -naphthol. *p*-Nitroaniline was diazotised in the usual way and coupled with 4-nitro- $\alpha$ -naphthol, dissolved in a strong solution of sodium carbonate. The colouring matter was crystallised from a mixture of nitrobenzene (1 part) and glacial acetic acid (4 parts) and obtained in brick-red needles, which melted with decomposition at 255°. It is sparingly soluble in alcohol, acetone, or acetic acid, but dissolves readily in nitrobenzene. It is practically insoluble in alkali, but dissolves in cold concentrated sulphuric acid, yielding a violet solution, from which it was obtained in a fine state of division by pouring into water (Found: N = 16.53.  $C_{18}H_{10}O_5N_4$  requires N = 16.56 per cent.).

*p*-Nitrobenzenehydrazo-4-nitro- $\alpha$ -naphthol,

—One gram of the finely divided azo-compound was warmed at 60–70° with 20 c.c. of alcohol and 1 c.c. of ammonia while a slow current of hydrogen sulphide was passed into the mixture until solution was just complete. Dilution with water precipitated the hydrazo-compound as a brown, amorphous mass, which was filtered, washed, and purified by extraction with acetic acid. The substance melts at 220°. It is readily soluble in alcohol, acetone, or acetic acid, but insoluble in ether. It dissolves in alkali with a bluish-green colour, which fades on exposure to air, a brick-red precipitate, which resembles the original azo-compound, being formed. The dyeing of wool was effected as with dinitrohydrazobenzene. The colour changed from violet to rose-red on exposure to air (Found: C = 56.11; H = 3.62; N = 16.32.  $\text{C}_{16}\text{H}_{12}\text{O}_5\text{N}_4$  requires C = 56.47; H = 3.52; N = 16.47 per cent.).

*p*-Nitrobenzenehydrazo-*o*-nitrophenol,

—*p*-Nitrobenzeneazo-*o*-nitrophenol (Hewitt and Mitchell, T., 1905, 87, 229) was prepared in a different manner by diazotising *p*-nitroaniline and coupling it with *o*-nitrophenol. It was then reduced in the same way as *p*-nitrobenzeneazo-4-nitro- $\alpha$ -naphthol. The crude hydrazo-compound was freed from unchanged material by boiling with benzene for a few minutes, and further purified by extraction with alcohol. The substance melts with decomposition at 260°. It is readily soluble in alcohol or acetic acid, insoluble in benzene, and dissolves in alkali with a fine blue colour. The alkali solution decolorises on exposure to air, leaving a brown precipitate. The dyeing of wool was effected as with the other hydrazo-compounds. The colour on exposure to air changed from violet to brown (Found: C = 49.51; H = 3.79; N = 19.61.  $\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_4$  requires C = 49.65; H = 3.44; N = 19.31 per cent.).

4-Nitronaphthaleneazo-4-nitro- $\alpha$ -naphthol,

—It was not found necessary to separate 4-nitronaphthylamine from the 2-nitro-aceto- $\alpha$ -naphthalide formed during its preparation (Liebermann, *Annalen*, 1876, 183, 229). Two grams of the mixture were diazotised in the ordinary way and the unchanged 2-nitro-aceto- $\alpha$ -naphthalide was removed by filtration. The use of ethyl nitrite in diazotisation (*loc. cit.*) is therefore not necessary. The solution of 4-nitronaphthalenediazonium chloride was coupled with 1 gram of 4-nitro- $\alpha$ -naphthol, dissolved in a solution of sodium carbonate. The dyestuff crystallises from a mixture of nitrobenzene (4 parts) and acetic acid (1 part) in brownish-red needles which

melt with decomposition at  $240^{\circ}$ . The substance is almost insoluble in alcohol, acetone, or acetic acid, but dissolves readily in nitrobenzene (Found: N = 14.34.  $C_{20}H_{12}O_5N_4$  requires N = 14.43 per cent.).

In conclusion, the author expresses his sincere thanks to Professor E. R. Watson for his kind encouragement and valuable suggestions.

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### CCCXLVII.—*Researches on Residual Affinity and Co-ordination. Part XIV. Interactions of Metallic Salts and Dimethyldithioethylene.*

By GILBERT T. MORGAN and WILFRID LEDBURY.

THE selective character of chemical affinity is manifested in the combination of the metals with oxygen and sulphur, respectively. The metallic elements may in this respect be divided roughly into two main series; one series, exhibiting a marked tendency to combine with oxygen, occurs in oxygenated minerals, whereas the other series shows a similar propensity for association with sulphur, the latter group being found in the natural sulphides. The line of demarcation is, however, not sharp, as several metals occur both in oxygenated minerals and in sulphides.

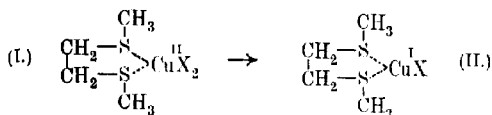
The researches described in this communication deal with a representative set of the metals combining preferentially with sulphur. On the current electronic theories of chemical combination, sulphides arise as a result of the sharing of electrons between the radicles of electropositive metals and electronegative sulphur, the latter element being uniformly bivalent in these combinations. There is, however, abundant experimental evidence for the belief that this interchange of electrons does not exhaust the possibilities of chemical combination. The metallic radicles and the bivalent sulphur atom each exhibit residual affinity: the former in their hydrated and ammoniated salts, the latter in such co-ordinated compounds as  $(CH_3)_2S \cdot ZnBr_2$  and  $2(CH_3)_2S \cdot PtCl_2$ .

Our results show that there is at least a qualitative relationship between the tendency for a metallic radicle to combine with sulphur by principal or electronic valency and its propensity to become associated with alkyl sulphides, the particular organic sulphide employed being dimethyldithioethylene,  $CH_3 \cdot S \cdot C_2H_4 \cdot S \cdot CH_3$ , a sub-

stance which functions co-ordinatively as a chelate group containing two associating units. The metals are considered in periodic order.

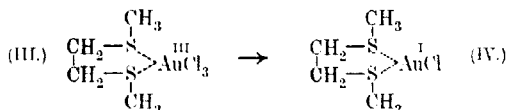
*Group I.—The Currency Metals.*

Cupric chloride and bromide combine in molecular proportions with dimethyldithiolethylene even in aqueous solution. The resulting dimethyldithiolethylene cupric haloids (I) show, however, a marked tendency to change into cuprous compounds (II), the instability being especially noticeable in the case of the dibromide.



The diminution in the valency of copper is accompanied by an alteration of colour as the dark green cupric compound changes to the white cuprous derivative. This reduction offers a close analogy to the change occurring in the precipitation of cupric salts by hydrogen sulphide, when the product consists partly of cuprous sulphide.

A similar parallelism is observable in the case of gold salts. Precipitation with hydrogen sulphide leads to reduction, the product containing only the lower gold sulphides. Auric chloride and the dithiol ether furnish yellow *dimethyldithiolethylene auric chloride* (III), stable only in the absence of moisture, which, in contact with water or moist solvents, undergoes reduction yielding white *dimethyldithiolethylene aurous chloride* (IV).



Owing to their highly associated character, the silver haloids could not be brought into combination with the dithiol ether even under pressure at 220°.

*Group II.—Metals of the Zinc Family.*

In this group of metals the stability of the sulphide increases with the rise of atomic weight; from magnesium sulphide, decomposed by cold water, to mercuric sulphide, which is extremely resistant to strong mineral acids. The co-ordination compounds of the zinc group with alkyl sulphides show a precisely similar change in stability. Combination was observed between magnesium

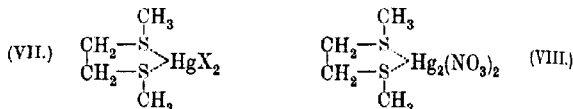
iodide and the dithiolethylene in anhydrous ether, but the product dissociates rapidly at the ordinary temperature.

*Dimethyldithiolethylene zinc bromide* (V) is more stable, but is decomposed by water or alcohol.

*Dimethyldithiolethylene cadmium iodide* (VI) can be prepared in aqueous solution, although the corresponding *bromide* and *chloride* are decomposed by water or moist solvents.



Considerably greater stability is observed with the *dimethyldithiolethylene mercuric haloids* (VII), and this stability increases from the chloride to the iodide.



X = Cl, Br, or I.

It is noteworthy that the interaction of the dithiol ether and mercurous nitrate is attended by the elimination of a considerable proportion of the mercury present as in the sulphide precipitation of mercurous salts, but on operating in the cold, a white, crystalline *dimethyldithiolethylene mercurous nitrate* (VIII) separates, which is, however, very unstable, water or moist solvents causing a separation of mercury. This tendency of the mercurous additive compound to shed a portion of the metal is reminiscent of many analytical reactions of mercurous salts.

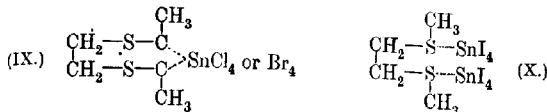
### Group III.

The rare metals of the gallium group were not tested with the dithiol, but Kurowski's observation (*Ber.*, 1900, 43, 1079) that thallous acetylacetone combined with carbon disulphide was reviewed in detail when it was found that the reaction with this thallous derivative and also with thallous benzoylacetone was not one of simple addition. In each case half the  $\beta$ -diketone radicle was replaced by a molecular proportion of the bisulphide. The orange-coloured products were, however, amorphous and very ill-defined, so that it was not possible to derive a rational formula for these substances.

### Group IV.

The stannic haloids combined readily with the dithiol ether and in the case of the chloride (IX) considerable heat was gener-

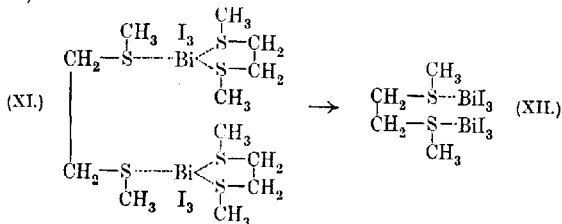
ated. This additive compound and the corresponding bromide (IX) show a different order of co-ordination from that indicated by the iodide (X).



It was not found possible to induce a combination of the dithiol ether with the more associated lead haloids.

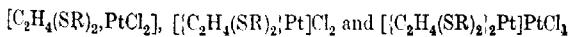
#### Group V.

The most striking result in this group was obtained with bismuth iodide, which gave rise to a bright scarlet crystalline *trisdimethyldithiolethylenedibismuthtri-iodide* (XI). The appearance of this co-ordination compound recalls a dry test for bismuth in which a compound of the metal after heating before the blowpipe with sulphur and potassium or cuprous iodide furnishes a scarlet incrustation stated to be bismuth iodide (Fresenius, "Qualitative Chemical Analysis," 1887, p. 150). The new red co-ordination compound is, however, very sensitive to light or moisture and, losing a portion of the dithiol ether, passes into dimethyldithiolethylene bismuth tri-iodide, a black substance of simpler type (XII).



#### Group VIII.

Of the transition elements, platinum had already been combined with dialkyldithiolethylenes by Tschugaeff and Kobljamski (*Z. anorg. Chem.*, 1913, **83**, 14), products of the following types

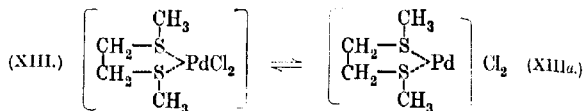


being obtained with each dithiol ether.

With potassium palladochloride, the dithiol ether furnished quantitatively only one product, the well-defined, crystalline *dimethyldithiolethylene palladous chloride* (XIII), from which the



corresponding *bromide, iodide, and nitrate* are obtainable by double decomposition. The hydroxide, produced in aqueous solution by the action of silver oxide, is distinctly alkaline, so that it is probable that the chloride exists at least partly in an ionised condition owing to the tendency for palladium to have a co-ordination number less than four.



#### Summary.

1. In certain instances the metallic radicles precipitated as sulphides in analytical practice give rise to well-defined co-ordination compounds with dimethyldithioethylene.

2. Whenever the analytical procedure tends to produce an alteration in the valency of the metallic radicle a similar tendency is observable with the dithiol derivatives; diminution in valency is noticed with copper and gold, whereas an exaltation of valency accompanied by partial elimination of metal is indicated in the case of mercurous salts.

3. Of the metals examined, those forming the most refractory sulphides furnish the most stable dithiol co-ordination compounds.

4. It may be concluded from these experimental results that the same selective affinity is at work between sulphur and the metallic radicles whether it is effective as principal valency in producing sulphides or whether it operates as residual affinity in the formation of co-ordination compounds.

#### EXPERIMENTAL.

##### *Preparation of Dimethyl Dithioethylene, CH<sub>3</sub>·S·CH<sub>2</sub>·CH<sub>2</sub>·S·CH<sub>3</sub>.*

Methyl mercaptan, the starting point in this research, was prepared conveniently by Arndt's method (*Ber.*, 1921, **54**, [B], 2236), in which thiourea is converted into methylthiourea sulphate, the latter substance being hydrolysed by 5*N*-sodium hydroxide into dicyanodiamide and methyl mercaptan (b. p. 5°). The volatile product was collected in a bulb tube, cooled with solid carbon dioxide and ether, and converted into its sodium salt by pouring into saturated alcoholic soda. To the alcoholic solution of sodium mercaptide in a reflux apparatus was added the calculated amount of ethylene dibromide. Considerable heat was generated, sodium bromide separated, and the double decomposition was completed

on the water-bath. The alcoholic mixture was poured into water, the heavy oil subsided, and a further amount was obtained by extracting the aqueous solution with ether. The crude dithiol was dried over anhydrous sodium sulphate and distilled, the fraction boiling at  $181.5-183.5^{\circ}$  being taken (yield 85 per cent., compare *Ber.*, 1871, 4, 716).

*Bisdimethyldithiolethylene Cuprous Bromide*,  
 $(\text{CH}_3\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_3)_2\text{Cu}_2\text{Br}_2$ .

On adding the dithioether (1.8 grams) to 3.2 grams of hydrated copper sulphate in 30 c.c. of water, the solution assumed a vivid emerald-green colour, but the oily thio-compound remained undissolved. The addition of 5 grams of potassium bromide in saturated aqueous solution caused a further colour change to dark olive-green and on continued agitation a brownish-white, crystalline substance slowly separated, the colour of the solution faded to light green, and the odour of the thioether almost disappeared. The product, after washing with alcohol, chloroform, and ether, was dried over sulphuric acid; it melted with decomposition to a clear liquid at  $161-162^{\circ}$  (Found: Cu = 23.94; Br = 30.25; S = 23.94.  $\text{C}_8\text{H}_{20}\text{Br}_2\text{S}_4\text{Cu}_2$  requires Cu = 23.95; Br = 30.12; S = 24.10 per cent.).

*Bisdimethyldithiolethylene cuprous bromide* separated in six-sided plates insoluble in water and the volatile organic media with the exception of pyridine, which dissolved the compound to a bright yellow solution, becoming olive-green on warming.

*Bisdimethyldithiolethylene Cupric Chloride* (Formula 1).

To a solution of 1 gram of cupric chloride in 10 c.c. of water was added 1 gram of the organic disulphide in alcoholic solution together with 4 c.c. of concentrated hydrochloric acid. The addition of a large excess of alcohol caused the cupric chloride additive compound to separate from the olive-green solution in very dark green, almost black, clusters of well-defined, glistening needles, which, after washing successively with absolute alcohol and dry ether, retained a faint odour of the organic sulphide (yield 0.4 gram). On long exposure, the compound assumed a grey tint owing to reduction from the cupric to the cuprous condition. It was appreciably soluble in absolute alcohol and separated from this solvent in dark green, acicular crystals, melting and decomposing at  $130-130.5^{\circ}$ . The compound was only sparingly soluble in the common anhydrous organic solvents (Found: Cu = 24.83; Cl = 27.59; S = 25.14.  $\text{C}_4\text{H}_{10}\text{Cl}_2\text{S}_2\text{Cu}$  requires Cu = 24.79; Cl = 27.68; S = 24.95 per cent.).

*Dimethyldithioethylene Bisaurous Chloride (Formula III).*

The thioether was added to a solution of auric chloride in water or in moist ether or alcohol so long as a yellow precipitate was produced. The mixture was then agitated until the colour of this precipitate changed to white, a brown, viscid material being formed as a by-product. The white product consisted of microscopic, rod-like crystals, which were dried over concentrated sulphuric acid (Found: Au = 66.85; Cl = 12.16.  $C_4H_{10}Cl_2S_2Au_2$  requires Au = 67.14; Cl = 12.09 per cent.).

This white co-ordination compound was only very sparingly soluble in alcohol and almost insoluble in other volatile organic media; it blackened without melting at 178–179°.

*Dimethyldithioethylene auric chloride* (formula IV) was obtained in agglomerates of small, orange-yellow, acicular crystals when the thioether was added to a solution of auric chloride in dehydrated ether. This yellow auric derivative was rapidly converted into the preceding aurous compound by the addition of water, but providing that all moisture was excluded it remained sufficiently permanent for analysis (Found: Au = 46.46; Cl = 24.90.  $C_4H_{10}Cl_3S_2Au$  requires Au = 46.33; Cl = 25.02 per cent.).

The dithiol auric chloride decomposed indefinitely at 70–75° and was decomposed by moist solvents.

*Dimethyldithioethylene Derivatives of Magnesium, Zinc, Cadmium, and Mercury.*

Dimethyldithioethylene magnesium iodide, which was produced by adding the thioether to anhydrous magnesium iodide in dry ether, separated in colourless crystals on concentrating the ethereal solution, but it decomposed so quickly into its generators even at the ordinary temperature that it could not be analysed.

*Dimethyldithioethylene zinc bromide* (formula V) was distinctly more stable than the preceding magnesium derivative; it was similarly prepared from carefully dehydrated materials. Powdered zinc (2 grams) and bromine (1.5 c.c.) were combined in 120 c.c. of dry ether. One gram of thioether was added to the filtered solution and after thorough mixing the liquid was evaporated and the residual oil left in the desiccator. Aggregates of small, hard, octahedral crystals separated and were washed with dry ether (Found: Zn = 19.19; Br = 45.92.  $C_4H_{10}Br_2S_2Zn$  requires Zn = 18.82; Br = 46.06 per cent.).

This co-ordination compound softened at 123° and melted to a clear liquid at 137°; it was decomposed at once by water and even by warm alcohol; it dissolved readily in ether or acetone, but its solubility in other organic solvents was very slight.

*Dimethyldithioethylene cadmium iodide* (formula VI) was sufficiently stable to be prepared in aqueous solution. Potassium iodide (5.47 grams) was added to 25 c.c. of warm water containing 5.08 grams of cadmium nitrate and 2.01 grams of thioether. The mixture was agitated, when a colourless, crystalline mass separated which, after cooling, was washed successively with water and alcohol. The cadmium compound was very soluble in warm alcohol and crystallised from this solvent in white, glistening needles melting at 168–169° and assuming a yellow tint on exposure to air and light (Found: Cd = 22.70, 23.12; I = 52.20; S = 13.04.  $C_4H_{10}I_2S_2Cd$  requires Cd = 22.95; I = 52.00; S = 13.11 per cent.).

The compound was readily soluble in methyl alcohol, but only slightly soluble in benzene or chloroform. The pure dry substance had a decided odour of the thioether, which was much more noticeable than in the case of the following mercury compounds. The corresponding thioether derivatives of cadmium chloride and bromide could not be prepared in aqueous solutions.

*Dimethyldithioethylene Mercurous Nitrate* (Formula VIII).—An immediate precipitation of metallic mercury occurred on treating a saturated aqueous solution of mercurous nitrate with a few drops of the organic disulphide. Further deposition of metal ensued on warming, but on cooling the filtered solution, which at this stage possessed a peculiar sweet odour, a hard, white, crystalline deposit began gradually to separate. These crystals consisted of very small, nacreous prisms matted together in wart-like incrustations. After its separation, the mercurous compound was not washed with water since this treatment caused the separation of mercury [Found: Hg = 62.47;  $NO_3$  (by reduction to  $NH_3$ ) = 19.11.  $C_4H_{10}S_2(NO_3)_2Hg_2$  requires Hg = 62.00;  $NO_3$  = 19.16 per cent.].

This mercurous additive compound, which was only sparingly soluble in organic solvents, melted and decomposed violently at 156.5°.

*Dimethyldithioethylene mercuric chloride,*

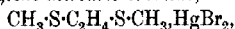


produced quantitatively on adding the calculated amount of thioether to a warm concentrated solution of mercuric chloride, separated in hard, colourless, prismatic crystals melting at 109° with decomposition (Found: Hg = 50.88; Cl = 17.91; S = 16.13.  $C_4H_{10}Cl_2S_2Hg$  requires Hg = 50.89; Cl = 18.10; S = 15.92 per cent.).

The compound was sparingly soluble in cold water, dissolved more readily on warming, but with dissociation; it was slightly

soluble in benzene, acetone, or chloroform, and more soluble in alcohol.

*Dimethyldithioethylene mercuric bromide,*



prepared by mixing warm solutions of potassium bromide and the preceding mercuric chloride compound (1 gram in 70 c.c.), separated from the filtered solution in colourless, acicular crystals; it was sparingly soluble in hot water or alcohol, but less dissociated than the preceding compound in these solvents; it melted at 115° (Found: Hg = 41.51; Br = 33.08.  $\text{C}_4\text{H}_{10}\text{Br}_2\text{S}_2\text{Hg}$  requires Hg = 41.49; Br = 33.16 per cent.).

*Dimethyldithioethylene mercuric iodide,*  $\text{CH}_3\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_3\cdot\text{HgI}_2$  obtained by a similar double decomposition from potassium iodide and the dithiol mercuric chloride compound, was sparingly soluble in hot water, but unlike the preceding mercury compounds it dissolved without dissociation. From warm alcohol, it separated in snow-white, matted needles, becoming yellow at 126–127° and melting at 134° with decomposition (Found: Hg = 34.32; I = 44.32.  $\text{C}_4\text{H}_{10}\text{I}_2\text{S}_2\text{Hg}$  requires Hg = 34.71; I = 44.04 per cent.).

*Dimethyldithioethylene Stannichloride,*  $\text{CH}_3\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_3\cdot\text{SnCl}_4$ .

On adding stannic chloride to excess of the thioether, the two liquids combined so vigorously that cooling was necessary. The product, a white, powdery mass, was freed from the organic sulphide by washing with cold chloroform; it dissolved in alcohol and separated therefrom, on evaporating, in a crystalline form. It melted at 209° with decomposition (Found: Sn = 31.05; Cl = 36.88; S = 16.71.  $\text{C}_4\text{H}_{10}\text{S}_2\cdot\text{SnCl}_4$  requires Sn = 31.08; Cl = 37.08; S = 16.67 per cent.).

This stannichloride, which was comparatively stable in the atmosphere, was readily decomposed by water; it dissolved in the ordinary organic media, but was crystallised only with difficulty owing to its extreme solubility.

*Dimethyldithioethylene Stannibromide,*  $\text{CH}_3\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_3\cdot\text{SnBr}_4$ .

Powdered tin was heated under reflux with a 12 per cent. solution of bromine in carbon tetrachloride until the colour of the bromine had disappeared, when to the filtered solution was added slowly the calculated quantity of the thioether, dissolved in carbon tetrachloride. A yellowish-white, crystalline precipitate separated which was very slightly soluble in chloroform, benzene, or carbon disulphide. On heating, it assumed a bright yellow colour and then melted with decomposition at 199° to a brown liquid. This

product dissolved readily in alcohol, acetone, or ethyl acetate, but was not reprecipitated from these solutions by chloroform or carbon tetrachloride (Found: Sn = 21.09; Br = 56.80.  $C_6H_{10}Br_4S_2Sn$  requires Sn = 21.20; Br = 57.07 per cent.).

Water decomposed this bromide slowly in the cold, more rapidly on warming.

*Dimethyldithioethylene Stanni-iodide* (Formula X).

Recrystallised stannic iodide, prepared by dissolving granulated tin in a warm benzene solution of iodine, was treated in this solvent with excess of the thioether, when a brown compound separated which was very soluble in organic media. At 93°, it assumed a yellow colour, and melted sharply at 100° (Found: Sn = 17.33, 17.05; I = 73.09.  $C_4H_4I_8S_2Sn_2$  requires Sn = 17.30; I = 73.84 per cent.).

*Trisdimethyldithioethylene Dibismuthtri-iodide* (Formula XI).

On adding the thioether to a solution of bismuth oxynitrate in dilute hydrochloric acid, no precipitate occurred although the solution assumed a transient yellow tint, but the introduction of potassium iodide solution caused the deposition of a bright scarlet, crystalline substance which, when collected and dried as rapidly as possible, melted at 85–87° (Found: Bi = 26.93, 27.05; I = 49.15.  $C_{12}H_{30}I_6S_6Bi_2$  requires Bi = 26.95; I = 49.36 per cent.).

This characteristic red co-ordination compound of bismuth was very sensitive to light or moist air, although dried specimens, when kept in sealed tubes in the dark, retained the red colour for a considerable time. Digestion with cold organic solvents led to the removal of two-thirds of the thioether with the formation of a black substance, *dimethyldithioethylene bismuth iodide* (formula XII) (Found: Bi = 32.56.  $CH_3\cdot S\cdot C_2H_4\cdot S\cdot CH_3\cdot 2BiI_3$  requires Bi = 32.25 per cent.).

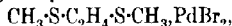
*Dimethyldithioethylene Palladous Chloride*  
(Formulae XII and XIII).

On agitating potassium palladochloride (2.9 grams) in 60 c.c. of water with 1.20 grams of the dithiol, a yellow precipitate appeared and the mixture was warmed to complete the reaction. The yellow product settled out completely (yield 96 per cent.), leaving a yellow, supersaturated liquid. The compound crystallised from hot water in short, lustrous yellow needles melting and decomposing at 234–235° (Found: Pd = 35.70, 35.56; Cl = 23.90.  $C_4H_{10}Cl_2S_2Pd$  requires Pd = 35.80; Cl = 23.70 per cent.).

The compound was appreciably soluble in hot alcohol, but reduction occurred and palladium separated; a slight decomposition occurred in aqueous solutions.

When added to a warm aqueous solution of *dimethyldithiolethylene palladous chloride*, silver nitrate produced an immediate precipitate of silver chloride, and the filtrate on concentration at the ordinary temperature yielded an extremely soluble, yellow, crystalline dithiol palladous nitrate, melting at  $162^{\circ}$  to a red liquid. Moist silver oxide became coated with silver chloride and the filtrate was distinctly alkaline, containing probably a complex soluble hydroxide. Aqueous ammonia decomposed the co-ordinated palladous chloride, setting free the dithiol and forming dichlorodiamminopalladium,  $(\text{NH}_3)_2\text{PdCl}_2$ , crystallising in yellow needles. Warm dry pyridine also decomposed the palladous chloride compound, liberating the dithiol. On cooling the solution, a colourless substance separated having approximately the composition  $(\text{C}_5\text{H}_5\text{N})_6\text{PdCl}_2$ ; this product lost pyridine when exposed in a vacuum desiccator over sulphuric acid and ultimately left a residue of dichlorodipyridinopalladium [Found: Pd = 31.75,  $(\text{C}_5\text{H}_5\text{N})_2\text{PdCl}_2$  requires Pd = 31.78 per cent.].

*Dimethyldithiolethylene palladous bromide*,



obtained on adding aqueous potassium bromide (1 mol.) to a hot aqueous solution of the preceding compound, separated as an orange-yellow precipitate consisting of small needles; it melted and decomposed at  $219\text{--}220^{\circ}$  (Found: Pd = 27.21; S = 16.15; Br = 40.92.  $\text{C}_4\text{H}_{10}\text{Br}_2\text{S}_2\text{Pd}$  requires Pd = 27.42; S = 16.45; Br = 41.18 per cent.).

This palladium bromide additive compound was less soluble than the chloride in organic solvents.

*Dimethyldithiolethylene palladous iodide*,  $\text{CH}_3\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_3\cdot\text{PdI}_2$ , separated as a dark red, crystalline precipitate on mixing molecular proportions of potassium iodide and the foregoing chloride in aqueous solution (Found: Pd = 22.01; I = 51.41.  $\text{C}_4\text{H}_{10}\text{I}_2\text{S}_2\text{Pd}$  requires Pd = 21.99; I = 51.61 per cent.).

The palladous iodide, which consisted of small, acicular crystals slightly soluble in boiling water or alcohol, melted with decomposition at  $204^{\circ}$ ; reduction to metallic palladium occurred in the latter solvent.

#### *Action of Carbon Disulphide on Thallous $\beta$ -Diketones.*

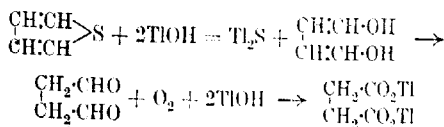
Kurowski observed that carbon disulphide, added to an alcoholic or benzene solution of thallous acetylacetonate, produced an orange-yellow, flocculent precipitate (*Ber.*, 1900, 43, 1079). The following

experiments showed that the reaction was not one of simple addition. To 1 gram of thallous acetylacetone (m. p. 155°), dissolved in 30 c.c. of absolute alcohol, were added a few c.c. of redistilled carbon disulphide, when the liquid slowly became turbid and deposited the orange precipitate. After a few hours, when no further precipitation was noticeable, the amount of insoluble compound was only 0.4 gram and the filtrate still gave the reactions of thallium acetylacetone. The reaction was not brought to completion even on adding a large excess of carbon disulphide. The product was amorphous and insoluble in the ordinary organic media. When digested with hot aqueous alkalis, the compound yielded a small amount of thallous sulphide. On heating, it blackened at 115° and evolved pungent vapours with no trace of carbon disulphide. Analyses of various preparations made in alcohol or benzene gave Tl = 69.10, 68.89, 68.80; S = 12.30, 11.99, 12.10 per cent. These data indicated that approximately half the acetylacetone had been replaced by carbon disulphide as in  $\text{Tl}_2\text{CH}(\text{CO}\cdot\text{CH}_3)_2\cdot\text{CS}_2$ , but it was impossible to arrive at a rational formula.

Thallous benzoylacetone and carbon disulphide reacted similarly, giving an orange, amorphous product, the analyses of which suggested a similar empirical formula,  $\text{Tl}_2\cdot\text{CH} < \begin{smallmatrix} \text{CO}\cdot\text{CH}_3 \\ \text{CO}\cdot\text{C}_6\text{H}_5 \end{smallmatrix} \cdot \text{CS}_2$ , but the substance was quite as ill-defined as that from thallous acetylacetone (Found: Tl = 62.99, 63.18; S = 11.04, 11.07 per cent.).

Thallous acetylacetone was decomposed by  $\alpha$ -thionaphthol, giving the yellow thallous salt of the latter reagent and free acetylacetone. Dilute alcoholic solutions containing thiophen and thallous acetylacetone in molecular proportions gave a yellow product similar to Kurowski's compound with carbon disulphide, but on allowing these reagents to interact in concentrated solution a small amount of thallous sulphide was precipitated, indicating a decomposition of thiophen.

With concentrated alcoholic solutions of thiophen and thallous hydroxide, black thallous sulphide was rapidly precipitated and the filtrate after exposure to the air yielded a small proportion of white thallous succinate, these results suggesting the following reactions:



in which the thionated cyclic system is completely broken down.



The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expenses of this investigation.

CHEMICAL DEPARTMENT,  
UNIVERSITY OF BIRMINGHAM,  
EDGBASTON.

[Received, November 7th, 1922.]

## WAR MEMORIAL.

Unveiling of the War Memorial to Lt.-Col. E. F. Harrison, C.M.G. and other Fellows of the Chemical Society on Thursday, November 16th, 1922, at 3 p.m., Sir JAMES WALKER, D.Sc., F.R.S., President in the Chair.

Sir JAMES WALKER: "We are met to witness the reception in trust by the Chemical Society of the Harrison Memorial and to take part in a simple ceremony—the dedication of a tablet in memory of Lt.-Col. Harrison and of those other Fellows of the Society who died in the service of their country during the Great War.

"Sir George Beilby, Chairman of the Harrison Memorial Committee, will make a statement of the origin and destination of the Memorial Funds, and I now call upon him to do so."

SIR GEORGE BEILBY: "Mr. President, My Lord, Ladies and Gentlemen,—We are gathered here to-day to take part in the unveiling of the memorial to those Fellows of the Chemical Society who made the supreme sacrifice during the Great War. It is my duty to relate to you how the memorial came to be erected, and to ask you to accept, on behalf of the Chemical Society, custody of this, and of an additional memorial, the nature of which I will describe. Among all those who knew the late Colonel Harrison, few better realised his intense, self-sacrificing energy, and his wonderful success in equipping our Troops with protection against poison gas than we, his colleagues upon the Chemical Warfare Committee. None can realise better than we that he gave his life in the service of the Country as truly and as willingly as those, who died on the field of battle. Shortly after his death we decided to endeavour to create some fitting memorial of his life and work. To this end we formed a Committee to invite subscriptions from those who had known and worked with him, and the sum collected



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has amounted, with accrued interest, to some £1,640. It was decided to use a portion of this money in the erection of a permanent memorial for which we felt no more appropriate home could be found than this building which houses the senior Society of the science which Harrison pursued. In agreeing to accept the custody of the memorial, your Society expressed a desire to combine with it a Roll of Honour of the remaining Fellows who lost their lives in the War. To this we willingly consented, and it has been possible to prepare a joint memorial harmonious in conception and in detail.

"With the balance of the sum collected, it was decided to create a fund to provide, every three years, a prize of approximately £150 to be awarded to the chemist, man or woman, not over thirty years of age, who shall have made the most meritorious original contributions to chemical science during the previous five years. The prize is to be awarded upon the recommendation of a Committee composed of the Presidents for the time being of the Chemical Society, the Society of Chemical Industry, the Pharmaceutical Society, and the Institute of Chemistry. It is to be given for distinguished research in any branch of chemistry, pure or applied, and no restriction is to be placed upon the manner in which the prize is to be utilised by the recipient. The Fund, the interest on which will provide the prize, will be held in trust, and administered by the Chemical Society. The subscribers to the Harrison Memorial Fund hope that this prize will do something to stimulate and encourage the younger chemical investigators, and we know that a purpose such as this is one that Colonel Harrison had ever foremost in his thoughts. The Prize and Memorial will be, we trust, appropriate tributes to his memory, recalling to the chemists of the future how gloriously he used their science in the cause of right and humanity.

"I ask you, Mr. President, to accept, on behalf of the Chemical Society, the custody of the Memorial affixed to the wall behind us, and of the Trust, the deeds and funds of which I now place in your hands."

SIR JAMES WALKER: "Sir George Beilby, on behalf of the Chemical Society, I gratefully accept the Trust which has been so generously offered to us by the Harrison Memorial Committee. It is a great satisfaction to the members of the Society to know that they have been entrusted with the care of the Memorial and with the administration of the Harrison Prize Fund. That part of the funds should be devoted to the institution of a prize for award to young chemists who have done meritorious research commends itself to us all as a most wise allocation. The capable

#### WAR MEMORIAL.

at the outset of his career is sufficiently provided for by stipends and grants, and late in life he generally has received (for the most part) some reward for his work. But there is a period in which the substantial encouragement of such a prize may well prove a determining factor in his development. The regulations for the award seem to have been framed with the utmost care and forethought. The Society considers it a high honour to have charge of the Memorial and to assist in the adjudication of the Prize. I thank you and your Committee in the name of the Chemical Society."

The President then called upon THE RIGHT HONOURABLE THE EARL OF CRAWFORD AND BALCARRES, K.T., P.C., who said :

"We are here to commemorate a small group of men connected with the branch of science specially represented by this learned Society—and in particular the service and sacrifice of Edward Harrison. These are occasions of melancholy retrospect, when we reopen the closed book; but none the less the record of public service, the acknowledgment of heroism, the recognition of exceptional skill and distinction do carry some small compensation, and let us hope cast a ray of comfort into the house of mourning.

"The Memorial presently to be unveiled is a tribute to 30 Fellows of the Chemical Society who lost their lives. Each name is there engraved, taking its apposite place in the Roll of Honour, and forming part of a striking work of art. May I say how much I rejoice that the Memorial itself should be a beautiful thing. How wise you men of science have been in choosing a sculptor of note, placing at his disposal an admirable and well-lighted site, giving him full freedom to develop his idea, and thus to conceive a monument which is a distinction to him, a credit to yourselves, and a worthy record of your deceased colleagues for all time.

"We do well to emphasise and perpetuate their memory. We do not ourselves forget their services, and we desire that posterity shall appreciate our veneration. We shall not act like those who disregarded the men of science in Ecclesiastes, the poor wise man who by his wisdom saved the city, and then was forgotten by those for whom he had done so much.

"The name of Edward Harrison stands out prominently amongst those of a gallant band called upon to protect, indeed to save our forces from the most terrible assaults ever directed by science against an army in the field.

"During the spring of 1915 our troops found themselves faced by the horrors of an unknown and inconceivable style of warfare. Science terrifies, but science also protects. There was a moment of incoherence, though let me say never a period of panic, when

mysterious agencies cast their death-warrant over our bewildered soldiers—a form of unseen aggression against which no remedy was known, and threatening the life of our armies, and with it the existence of our nation, with an unspeakable cataclysm.

“A few months later our science asserted its mastery. British science kept pace with German aggression, and I believe outstripped it. Somebody, I know not who, detected the genius of Harrison, rescued him from military duties where his special powers were being wasted, and by the autumn of 1915 he was laying the foundation of a huge organisation ultimately destined to become one of the central factors of victory.

“Though I never had the honour of meeting Colonel Harrison, I well recall a curious tumbledown little group of huts where experiments were conducted. It was difficult to penetrate into that out-of-the-world enclave, but I had occasion from time to time to see what was going on, and to share the obscure enthusiasm which prevailed among threatened men that something concrete was being done to stave off the impending danger. Poison gas was indeed our most implacable foe, and its intangible horrors the most subtle as well as the most lethal of all engines of war.

“From what I can learn Edward Harrison possessed the power of concentrating the accidents of knowledge and intelligence, directing them into a consistent and specific channel. He had the power of interrogation, combined with premonitions, intuitions, which enabled him to anticipate developments, and thus to meet in good time, sometimes in advance, the progress of enemy attacks.

“He takes his place among those illustrious men, from Jenner down to Lister, whose achievements in the noble efforts of prophylaxis confer incalculable fame upon British science.

“But it is not only Harrison to whose achievement we do honour to-day. Here I have a list of young Fellows of the Society, men of conspicuous ability in their own departments of research, men of character and promise, whose precious lives were prematurely ended. These, too, performed their part, each and all animated by the same motives of duty and patriotism—devoting themselves and ultimately sacrificing their lives in defence of all that we hold most sacred and most dear.”

The EARL OF CRAWFORD AND BALCARRES then unveiled the Memorial, and after the Last Post had been sounded, followed by one minute's silence and the Reveille, the PRESIDENT said :

“The sound of the bugle has announced the completion of to-day's ceremony and has recalled us from sorrowful reflection on the days of the Great War to the ordinary business of life. Please God, neither we nor our children shall again see a time in

which our patriotic duty and our common humanity shall be so at variance.

"It only remains for me to thank the Earl of Crawford for performing the unveiling of the Memorial and for the eloquent and touching words of his address. That Lord Crawford was First Commissioner of Works, and thus responsible for the fabric in which the Memorial stands, is the least of his qualifications for the task. As an artist and a writer on sculpture, he is peculiarly fitted to judge of the artistic merit of the Memorial, but what must appeal to us most is that he enlisted as a private in the R.A.M.C. and saw with his own eyes the ravages of poison gas and the success of the protective measures employed against it.

"Lord Crawford, on behalf of the Chemical Society and of the contributors to the Harrison Memorial Fund, I convey to you our most grateful thanks for your kindness in performing to-day's ceremony."

## OBITUARY NOTICES.

JAMES ROBERT APPELYARD.

BORN 1870; DIED OCTOBER 1921.

JAMES ROBERT APPELYARD was born in Bradford in 1870 and was the only surviving son of Mr. Rufus Bentley Appleyard, a schoolmaster of that town. He was educated at his father's school and subsequently took the regular course in chemistry and dyeing at the Bradford Technical College. In 1899 he was appointed assistant to Professor Percy F. Frankland at Dundee, where he subsequently also gave the lectures on dyeing and allied subjects. Ten years later he was appointed Lecturer on Dyeing at the Salford Royal Technical Institute, becoming later the Head of the Applied Chemistry Department, which position he occupied up to the time of his death.

While still at Bradford, Mr. Appleyard carried out work in collaboration with others on the quantitative estimation of picric acid, on the composition and properties of Tussah silk, and on the absorption of acids and bases by certain textile fibres, the results of which were published in the *Journal of the Society of Dyers and Colourists*. Subsequent work on which he was engaged was of a more strictly scientific character and included a paper on "Salts of Glyceric Acid; Influence of Metals on the Specific Rotation of Active Acids" in collaboration with Professor Percy Frankland (T., 1895, 67, 296), and in collaboration with Professor James Walker, papers on "Etheral Salts of Ethanotetracarboxylic Acid"

(T., 1895, 67, 768), "Transformation of the Alkylammonium Cyanates into the Corresponding Ureas" (T., 1896, 69, 193) and "Absorption of Dilute Acids by Silk" (T., 1896, 69, 1334). In collaboration with Mr. J. B. Deakin he contributed a paper on "The Action of certain Inorganic Sulphur Compounds on Cotton" (*J. Soc. Dyers and Col.*, 1902, 128), whilst his last contribution (with Mr. R. C. Jefferson), which was also technological in character, was on the "Rate of De-sizing of Cotton Cloth" (*ibid.*, 1915, 153). During the past fifteen years most of Mr. Appleyard's spare time was taken up with industrial investigations and consulting work.

An excellent teacher and of a genial disposition, Mr. Appleyard was beloved by his students and all who knew him. Although he had been in failing health for some years prior to his death and had latterly not been able to carry out his full duties, his interest in the subject was maintained to the end. His loss will be felt not only by his numerous friends and past students, but also by the industry which he represented, for which he had given of his best. He leaves a widow and an only son.

E. KNECHT.

#### ADRIAN BROWN.\*

BORN APRIL 27TH, 1852; DIED JULY 2ND, 1919.

ADRIAN BROWN was the junior member of the very remarkable amateur scientific quartette, Peter Griess, Cornelius O'Sullivan and the brothers Brown—Horace and Adrian, once active in the scientific service of brewing at Burton-on-Trent.

The amateur scientific worker is a peculiarly British product: he hates drill and grows through force of example, not of precept; he has not matured in countries where drill has been in the ascendant. Griess was an outstanding example. He spent six or seven years at the University—doing nothing as a formal student; the saying goes, that he wasted his time. Far from this—whilst he took his fill of student life, what to-day would be called his subconscious mind was clearly at work and he suddenly displayed extraordinary activity in the laboratory. His great ability was appreciated by Kolbe, his teacher, himself a man of the highest intelligence, to some extent trained here, under the late Lord Playfair, as fellow worker with the late Sir Edward Frankland, the ablest chemist of his time in the laboratory and the author of the theory of valency upon which our entire system of structural formulæ is based. Kolbe recommended Griess to Hofmann, then Professor at the

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Royal College of Chemistry, in Oxford Street, London—whence arose the dyestuff industry, as the outward and visible sign of the great leader's activity and example as an original worker. Griess brought with him from Germany his discovery of the diazo-compounds, one of the most remarkable in the history of chemistry, as it involved recognition of the fact, that nitrogen, up to that time regarded as an inert element, could form compounds of unusual chemical activity and extreme instability. He developed his discovery in London, until in 1862 he became assistant in Allsopp's Brewery in Burton-on-Trent. Here, until his death in 1888, he occupied an anomalous position, living a life all but apart from the brewery, an indefatigable worker, high up in an empyrean of constructive organic chemistry. Apparently, Griess did nothing in particular for brewing, beyond assaying its products; but he laid the foundation of a branch of the dyestuff industry which has since been the most remunerative of its many activities. His services were once sought by an English dyestuff firm but the beggarly terms offered him were naturally declined and we lost an irrecoverable opportunity.

In the past, scientific workers had their individual patrons who supported their inquiries; but the Allsopp firm behaved to their chemist in a way which is without parallel in the history of industrial enterprise; they seem to have gloried in having so distinguished a man on their staff, without considering the direct value of his services. His presence was testimony to their breadth of view, as well as to their liberality; they undoubtedly gained in repute from their action.

Horace Brown entered on his technical career, in 1866, at the time when Griess took up the position of chief chemist, at Allsopp's, vacated by Dr. Böttinger, father of the Dr. H. von Böttinger, recently deceased, who is noted for the part he played in the development of the German Dyestuff Industry. He had been influenced, as a lad, both by Böttinger and by Griess, but his only didactic training in chemistry was a year spent at the Royal College of Chemistry, partly under Hofmann and partly under Hofmann's successor, Frankland.

Cornelius O'Sullivan went to Burton in 1867. He too had been a pupil of Hofmann, at the Royal College of Chemistry; he was one of the assistants in the laboratory at the time when Horace Brown and the writer entered as students. He accompanied Hofmann to Berlin but, after a few months, on his recommendation returned to England to enter the service of Messrs. Bass and Co. An accomplished worker, he began the study of the mash-tun by

investigating the action of the enzymes of malt (diastase) on starch; he may be said to have rediscovered maltose in the course of this work and to have established its significance as a fundamental unit in the complex starch molecule. Although others have followed in his footsteps, to the present day we remain ignorant as to the precise nature of the successive changes which the starch molecule undergoes on hydrolysis and of the number of enzymes concerned in the process. O'Sullivan was also the first to study, in detail, the rate at which cane-sugar was hydrolysed by yeast invertase. Finally, he undertook an inquiry into the products of the hydrolysis of gum-arabic and laid solid foundations which no one yet has built upon.

Adrian Brown did not enter the scientific service at Burton until 1873, when its foundations had been deeply laid: he then spent several years studying for the distinguished part he was to take in the quartette.

He was born at Burton on April 27, 1852. He came of a practical and nature-loving stock. His father, Edwin Brown, the son of a small builder, left school at an early age, to become clerk at a private bank in Burton, ultimately the Burton, Uttoxeter and Ashbourne Union Bank, of which he was manager during the last twenty-five years of his life. He died suddenly, in 1876, at the age of fifty-seven. He was an ardent naturalist, specially known as a coleopterist, with a strong scientific bent and leanings to all the sciences, particularly geology.

He is referred to in the "Life and Letters of Charles Darwin" in a letter from Henry Walter Bates, the celebrated Amazonian traveller, to Darwin, dated October 17, 1862:—

"Mr. Edwin Brown is manager in a large Bank at Burton. I have known him twenty-one years; he was my earliest naturalist friend. I have always looked on him as a man of extraordinary intellectual ability. I have given him my notices on Carabi. He is amassing material (specimens) at very great expense. He has never travelled; this is a great deficiency, for the relation of species to closely allied species and varieties cannot, I think, be thoroughly understood without personal observation in different countries."

In the memoir, by Mr. Edward Clodd, prefixed to the reprint of the unabridged edition of "The Naturalist on the River Amazon," published by Mr. Murray, in 1892, it is stated that:—

"Bates was born at Leicester in 1825 and spent his youth

in the district. Apprenticed to a hoisery business, he left it soon after his master died and eventually entered Allsopp's Brewery as a clerk."

Mr. Clodd adds :—

"As often as he could he escaped from the desk to the open air, and some results of his entomologising are found in a paper on 'Coleoptera in the neighbourhood of Burton-on-Trent,' published in the *Zoologist* (VI, 1848, 1897). Mr. Edwin Brown, who obtained him the situation at Allsopp's, is referred to as the captor of several species scheduled in the paper."

Edwin Brown appears to have exercised considerable influence upon the fortunes of both Bates and A. R. Wallace. Bates became acquainted with Wallace at Leicester, where the latter was English master in the Collegiate School. Mr. Clodd tells us that :—

"The two friends often discussed schemes for going abroad to explore some unharvested region and at last these took definite shape, mainly through the interest excited by a little book, published by John Murray in 1847, entitled 'A Voyage up the River Amazon, including a Residence at Para,' by Mr. W. H. Edwards, an American tourist."

The writer learns from Dr. Horace Brown that this book had greatly interested his stepfather, Edwin Brown, who lent it to Bates to read. The recovery of such a fragment of history will not be without interest, as giving a clue to the mental process whereby the two travellers were eventually led to the study of problems of world-wide significance.

Adrian Brown was therefore nurtured in a scientific atmosphere. He attended the local grammar school, but his effective training was at the hands of his father and, in chemistry particularly, of his elder brother, Horace. He received his special technical training mainly at the Royal College of Science, the combination of the Royal College of Chemistry, Oxford Street, with the Royal School of Mines, Jermyn Street, then just effected at South Kensington. On leaving, he became private assistant to Dr. Russell, Lecturer on Chemistry in St. Bartholomew's Hospital Medical School.

In 1873 he quitted London for Burton, to act as chemist to Messrs. Salt and Co., Brewers.

In referring to the Burtonian quartette, which Adrian Brown was the last to join, as amateur workers, the writer is not unmindful

of the fact that all were brewers' chemists and therefore professionally engaged, excepting, perhaps, Griess—and it has always been thought that he has not had sufficient credit for the work he did in the brewery. None the less, the spirit in which they worked was that of the amateur of the past: they sought neither gain nor applause: love of their art, was their guiding light; they were led solely by desire to explore its fields, to grasp its value, to display its beauties.

Adrian Brown remained twenty-five years in the brewery, leaving in 1899 to take charge of the newly founded Chair of Brewing and Malting at the Mason College, Birmingham. When the University of Birmingham was established, he became Professor of the Biology and Chemistry of Fermentation and Director of of the School of Brewing. He died suddenly on July 2, 1919, three days after his wife.

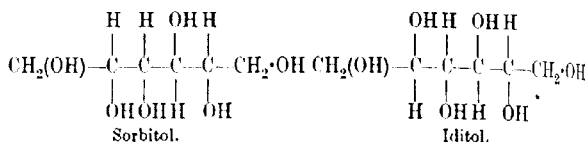
A naturalist from his birth upwards, a man of unobtrusive manner but great personal charm, he gained the esteem of all whom he met officially and the affection of his many friends. Not only was his standard of endeavour ever the highest but all he did was characterised by originality, great independence of judgment and a consistent logic.

He was not elected into the Society until 1911. His first work was in advance of the time and did not receive the attention it deserved, although the subject, the action of oxidising organisms, was one of great interest, oxidation playing so determining a part in vital activity. He began by studying the action of the well-known *Bacterium aceti*, used in producing vinegar from alcohol; then that of another organism, *Bacterium xylinum*, which he was the first to isolate from "Mother of Vinegar."

The point brought out in the earlier inquiry was the inability of *B. aceti* to condition the oxidation of methylic alcohol, although it grew in presence of this compound: then, that it was able to determine the conversion, not only of ethylic alcohol but also of propylic, to the corresponding acid: yet was without action on isopropylic and isobutylic alcohols: still, it grew in the presence of these compounds but was killed by fusel oil and amylic alcohol. These remarkable differences in behaviour of compounds so closely related remain unexplained to the present day. Assuming that oxidation be determined by a catalyst, *i.e.*, at a solid surface, it is most probable that the surface is differently affected by the different alcohols: but on any hypothesis the fact that methylic and isopropylic alcohols are unattacked, whilst compounds so close to them in all chemical properties are oxidised, is very striking; no other such marked instance of bacterial epicurism is known.

The results of his work on *B. xylinum* were of less direct significance, as his attention was mainly directed to the membrane which this organism produces in sugar solutions; he thought it was a variety of cellulose but from later work, by Emmerling, it is probable that the product is of a chitinous character. Here again, however, a field is opened up for further inquiry—if action take place within the cell, how comes it that such a product is secreted without the organism if this be not destroyed in the process?

The activities of *B. xylinum* were studied, a few years later, by the French chemist, Bertrand, who established the fact that it has an entirely remarkable discriminative power, as in compounds sensitive to its oxidising influence two  $\text{H}\cdot\text{C}\cdot\text{OH}$  groups are present, not only in conjunction but so placed that the two OH groups in these are on the same side of the plane in the formula; thus when the two isomerides formed by reducing sorbose are submitted to the action of the organism



sorbitol alone is oxidised and reconverted into ketose (sorbose). It is in no way clear, at present, whether the selective activity displayed by the organism be that of an enzyme or traceable merely to a peculiarity in the oxidative process.

The root ideas underlying our present conception of the nature of enzymic hydrolysis are largely traceable to Adrian Brown's iconoclastic work. Beginning with observations on the rate of reproduction of yeast cells, he noticed that a constant amount of yeast fermented an approximately *constant weight* of sugar, in unit time, in *solutions of varying concentration*; the graph of his experiments was a straight line, not a logarithmic curve—indicating the change of regularly diminishing amounts in successive unit periods—such as was held to be expressive of the simple enzymic change conditioned by invertase, on the basis of the experiments made by Cornelius O'Sullivan and Tompson, published in 1890. Hence he was led to re-examine the evidence adduced by these chemists, in support of their view, that the enzymic change was a mass-action effect, strictly comparable with the changes taking place in solutions of crystalloids—in other words, that enzymic change took place in solution.

He dealt with this subject in an exhaustive manner. The conclusion arrived at was, that during the earlier period of change, as in fermentation, the sugar is hydrolysed at a linear rate, the amount converted being practically independent of the concentration of the solution, in no way proportional to it. The rate of hydrolysis is much reduced by the addition of invert-sugar, that is to say, of the products of change; lactose, except in very large proportion, however, has little effect.

These conclusions have been fully confirmed by later inquiries. It may now be taken as established, that enzymic action is effected at solid surfaces. Complete confirmation of this explanation has been given by recent observations on the action of a catalyst such as finely-divided metallic nickel in determining the hydrogenation of the fatty oils.

Much of Adrian Brown's work was in criticism of Pasteur's findings, especially the great Frenchman's conclusion that fermentation was life without air; he thought that he had proved the contrary. He studied the effect of alcohol and found that it greatly retarded the reproductive growth of yeast; also the effect of carbon dioxide but came to the conclusion that, as it had no greater influence than hydrogen and as there was a much larger increase in presence of air, the repression of growth was due to exclusion of oxygen. He was, therefore, led to favour the conclusion that reproductive growth of the yeast cell, under ordinary anaerobic conditions, is determined by the amount of oxygen at the disposal of the organism prior to the commencement of reproduction.

Recently, however, Slator, working in the laboratory of Messrs. Bass and Co., thought he had proof that not only has carbon dioxide a greater influence than has been supposed on the activity of the yeast organism but also that oxygen is not required for reproductive growth of the cell—thereby upholding both a common opinion of carbon dioxide and Pasteur's view as to oxygen being unnecessary. Later observations have shown, he admits, that he had not sufficiently removed the oxygen.

It remains to consider what is undoubtedly his most remarkable work—that on diffusion into the barley corn, noteworthy both on account of the beauty and delicacy of the method he developed and the significance of the results. Having eyes to see as well as an inquiring mind, he was led to take special notice of the blue layer just below the skin in certain varieties of barley. Desirous of finding out what happened, in the malting process, when barley was steeped in water, as it is during the preparation of malt, also what would be the influence of impurities in the water, he first studied the behaviour of dry barley-corns in water and then in

various solutions. He saw that in blue barley he had a perfect mechanism for the quantitative study of diffusion phenomena. The blue layer furnished the discriminating membrane; the finely granular mass of starch within the corn served to attract water into the grain. By placing a set of weighed corns in water and at intervals removing them and determining the increase in weight, at various temperatures too, the rate at which water entered was easily ascertained. The variation in the rate at which it accumulates in the grain, as the temperature is raised, was in agreement with that at which the vapour pressure of water rises when this is heated.

A similar tale is told by solutions of most salts and of substances such as the sugars—these all have vapour pressures lower than that of water and water accumulates less rapidly in barley corns placed in these solutions than if they were in water, the rate depending on the concentration.

Solutions of the ordinary strong acids and alkalis also give up water to dry barley corns and become concentrated but no acid passes across the discriminating membrane; the blue colour remains unchanged in all sound corns.

But weak acids, also weak alkalis, such as ammonia, readily pass through; moreover, the membrane is penetrable by all chemically neutral substances at all soluble in water—such as acetic acid and its homologues, chloroform, even hydrocarbons such as benzene. These all pass into the corn together with water and actually accelerate the passage of water into the grain. It is no question of molecular size: such molecules do not penetrate the membrane because of their smaller size; on the contrary, butyric acid enters more rapidly than acetic and the alcohols of the ethylic series pass through the more rapidly the greater their molecular weight, so long as they are reasonably soluble in water.

Eventually an equilibrium is reached within the corn and the concentration of the solution may become higher than in the liquid outside; it has even been observed, in the case of phenol and aniline, that the internal solution is "supersaturated." To take an example, when the corns are saturated in a solution containing 50 per cent. of acetic acid, the solution within contains 80 per cent. of the acid—but this is the limit, no more passing in from stronger solutions.

Previous observers on the passage of such substances through living tissues have correlated their relative activity and their lethal power with the solubility in fats and have postulated the existence of a lipoid layer at the tissue surfaces. Adrian Brown's

observations justify us in putting aside all such fancy explanations—the correlation is of consequence only in so far as the solubility referred to of substances in oils and fats is usually the converse of their solubility in water.

A full discussion of the work Adrian Brown accomplished and its bearing on contemporary inquiries, by the writer, is published in the *Journal of the Institute of Brewing*, 1921, vol. 27, pp. 197-260. From the point of view advocated in the present notice, his exemplary career and achievements merit most careful attention. His genius lay not on the surface but was manifest in a continuity of effort which, in sum, was remarkably effective. His work was an expression of himself: it came from within; but that he was induced, if not forced, to display his genius owing to the influence of the conducive environment in which he was placed is probably a not unwarrantable conclusion. Chamber music such as the Burtonians have discoursed so successfully might well and should be more cultivated, not only in industry but in the new Universities, even at Oxford.

H. E. A.

#### WILLIAM GOWLAND.

BORN DECEMBER 16TH, 1842; DIED JUNE 10TH, 1922.

PROFESSOR WILLIAM GOWLAND, F.R.S., Emeritus Professor of Metallurgy at the Royal School of Mines, died on June 10, in his eightieth year. By his death Metallurgy has lost one of its most learned and authoritative exponents, and a man of singular personal charm and distinction. It is interesting to notice that, like his predecessor at the Royal School of Mines, he had intended to enter the medical profession. Whereas Percy, however, completed his course of instruction and practised professionally for some years, Gowland, after working with a medical man in Sheffield for three years, abandoned this work and became a student at the Royal College of Chemistry. From there he passed, in 1868, to the Royal School of Mines, and two years later obtained the Associateship both in mining and metallurgy. He was awarded the Murchison medal in geology and the De la Beche medal in mining.

Gowland's first post was that of chemist and metallurgist to the Broughton Copper Company, Manchester. Two years later, he accepted an invitation to the Imperial Mint at Osaka, Japan, where he held the post of chemist and metallurgist for six years. During the next eleven years he acted as assayer, metallurgist,



and chief of the Foreign Staff at Osaka, and was for some time adviser to the Imperial Arsenal. His work was of a decidedly varied nature, and he did much to introduce Western metallurgical and chemical methods into the departments with which he was associated. Indeed, during this period, work of a chemical nature predominated. It was at this time that he acquired the knowledge of Japanese methods of extracting, refining, and working metals, for which he subsequently became so famous. In addition, he carried out exploration work in Korea on behalf of the Japanese Government, which was by no means free from danger to himself and his party. As a young man, Professor Gowland was a keen oarsman, and was the first to introduce rowing into Japan. The use of the wheel-barrow was unknown in the country. He provided with wheel-barrow the labourers who were engaged on some excavation work in the Copper Mint. The Japanese, however, did not appreciate this form of mechanical transport, and very quickly removed the wheels, preferring to carry the barrows, loaded, on their backs. During his residence, he built up a very fine collection of Japanese art, which included some valuable *kakemonas*. On leaving the country in 1889, the order of "Chevalier of the Imperial Order of the Rising Sun" was conferred on him by H.I.M. the Emperor of Japan, personally. Until the time of his death, he maintained his connexion with Japan, where he was held in very high esteem, and his London house became the Mecca of Japanese metallurgical students who visited this country.

After his return to England, Professor Gowland acted as chief metallurgist to the Broughton Copper Company for some years. In 1902, however, he entered the academic side of metallurgy, and was appointed Professor at the Royal School of Mines, in succession to the late Sir William Roberts-Austen. This post he held for seven years and retired in 1909, although he again filled his post at the School during an emergency in the Session from 1912 to 1914. It is remarkable that a man should enter on what must after all have been a new profession in his sixtieth year, and have made such a success of it. He was extremely thorough in everything that he undertook. His lectures were very carefully prepared and admirably delivered. He had a gift of clear and trenchant exposition. Staff and students found in him a man of his word, who took deep interest in their welfare and was ready to give of his time ungrudgingly in their service.

So far as metallurgy is concerned, his chief interest lay in the metals copper, silver, gold, lead, and their alloys. His knowledge of the metallurgy of copper in particular was unique, based as it was on experience of the best methods in vogue both in the East

and West. In 1914 he published a text-book on the metallurgy of non-ferrous metals, which quickly became recognised as an authoritative work on the subject, and is now in its third edition. He also contributed various papers to the Institution of Mining and Metallurgy, the Chemical Society, and the Society of Chemical Industry. In 1907 he was elected President of the Institution of Mining and Metallurgy, and in 1909 was awarded the Institution's gold medal. He was an original member of the Institute of Metals, founded in 1908, and became its third President and its first May Lecturer.

There was, however, another side to Gowland's intellectual interests, as shown by his membership of the Society of Antiquaries, the Royal Anthropological Institute, and the Numismatic Society. His publications under these heads were numerous and varied, dealing with, for example, the early metallurgy of lead and silver, the remains of a Roman silver refinery at Silchester, silver in pre-historic and proto-historic times, and the burial mounds and dolmens of the early emperors of Japan. From 1905 to 1907 he acted as President of the Royal Anthropological Institute.

During the last seven years of his life Professor Gowland, who did not escape the infirmities of advancing age, was very much confined to his room. He was, however, a man of indomitable spirit and maintained his intellectual activity and catholicity up to his death. He endeared himself by his personal qualities to a wide circle of friends, by whom he will always be affectionately remembered.

H. C. H. C.

#### PROF. PHILIPPE A. GUYE.\*

BORN JUNE 12TH, 1862; DIED MARCH 27TH, 1922.

By the death of Prof. Philippe Auguste Guye, on March 27, Switzerland loses one of the most eminent of her savants, and the world of science is the poorer by the passing away, in the full maturity of his intellectual powers, of an assiduous and successful cultivator of natural philosophy, distinguished alike for the range and profundity of his knowledge, the force of his genius, for his originality, his ingenuity and remarkable experimental skill. Geneva has long been a home of science; some of her citizens are among the most honoured of its votaries, and Guye now assumes his due position in a roll already made illustrious by the names of Saussure, De La Rive, and Marignac.

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Philippe A. Guye was born at Saint-Christophe (Vaud) on June 12, 1862. His earliest scientific studies were made at the University of Geneva, where he worked under Graebe, with whom he published papers on diphthyl and on naphthalene hydrides—a modest enough theme for the 'prentice hand—mainly a repetition of Graebe's observations of ten years previously, which seemed to have been called in question by the subsequent work of Agrestini. After taking his doctorate he repaired to Paris, where he remained some years, working in the laboratory of Friedel. Here he appears to have come under the influence of ideas on spatial chemistry which science owes to Le Bel, and much of his work during the next few years was devoted to their development. In 1892 he was recalled to Geneva to occupy the chair of theoretical and applied chemistry in the university of that city, to which he remained attached for thirty years. During this period Guye, by his energy and personal influence, his organising power, and the catholicity of his scientific aims, made an indelible impression on the academic life and activities of the university. He surrounded himself with a body of earnest and enthusiastic workers, attracted from all parts of the world, to whom he gave freely from a wealth of ideas which ranged over every department of chemical and physical science. It is estimated that upwards of 600 communications emanated from the Geneva laboratory while under his direction, some 200 of which bore his own name alone, many others being joint contributions by himself and his pupils. His own work was characterised by a rigorous sense of accuracy, by caution and a recognition of possible sources of error, amounting almost to intuition, combined with a capacity for generalisation and a *flair* for fruitful hypothesis which seemed, at times, like divination.

Although Guye began his scientific life under the guidance of Graebe, and at a time when the theory of organic chemistry and its technical applications were developing with extraordinary rapidity and success, systematic organic chemistry of the type with which the name of his eminent teacher is associated had few attractions for him, and it is doubtful whether Graebe's teaching and example had any permanent influence on his career. At all events, on his election to the Geneva chair he embarked upon the long series of investigations on problems of physical chemistry on which his fame mainly rests. He was early attracted to the many issues to which the molecular theory of van der Waals gave rise. He discovered a series of new relations between the physical constants of liquids and their molecular magnitudes, and he greatly extended the conception of molecular association in liquids. He devised new methods of determining the molecular weights of substances in the liquid

state and at the critical point. He attacked the study of molecular dissymmetry, and traced the connexion between optical activity and homology in liquids, between isomerism of position and rotatory power, and with the aid of his pupils he accumulated a great mass of experimental material which served to extend and substantiate his generalisations.

In 1903 Guye turned his attention to the study of atomic weights, and, in particular, to a critical examination of the experimental basis upon which these magnitudes rest. He thereby followed and perpetuated a tradition with which the fame of the Geneva school of chemistry, as personified by Marignac, will always be connected. Practically the greater number of the one hundred contributions to the literature of chemistry which we owe to Guye's pen during the past twenty years are devoted to this subject, upon which he lavished all the powers of his matured intelligence, his experience, ingenuity and manipulative skill. Thanks to his organising capacity and the ability and enthusiasm of his collaborators, we have been furnished with a series of fiduciary values which are probably among the best determined of physical constants, in which every known source of error has been rigorously scrutinised, and, as far as possible, eliminated. Naturally the trend of modern developments of ideas concerning the essential nature of the elements, and their fundamental relations and possible interdependence, attracted Guye's alert intelligence, and at the Brussels meeting of the International Conference in June last he pointed out their significance in connexion with the proposed reorganisation of the work of the International Committee on Atomic Weights, of which he was an enthusiastic advocate, and on which, had he lived, he would certainly have made his influence felt as a member.

It might be supposed from Guye's mental characteristics, and from the nature of his studies, that he would have little sympathy with the technical applications of chemistry. No such surmise could be further from the truth. Although not a professed technologist, he had a considerable knowledge of manufacturing chemistry, and he enjoyed the confidence and esteem of the leaders of chemical industry throughout Switzerland, to whom he was always accessible, and by whom his counsel and advice were highly appreciated. His name will always be associated with the extraordinary development of electrochemical synthesis in Switzerland, to which his lectures and writings largely contributed.

Guye exercised great influence in scientific circles in Geneva, and took a leading part in the organisation of Swiss science. He presided over the Swiss Physical and Natural History Society, was a member of the central Committee of the Helvetic Society of Natural

Sciences, and president of the Swiss Chemical Society and of the Council of Swiss Chemistry. In 1903 he established the *Journal de Chimie physique*, in which the greater number of the communications from his laboratory after that year were published, and he was mainly instrumental in placing *Helvetica Chimica Acta*—now the leading chemical journal in Switzerland—upon a sound and permanent foundation.

Guye's merits as a man of science were widely recognised. He was a member of the Scientific Academies of Petrograd, Madrid, and Bucharest, and honorary member of the Chemical Societies of France and England, a corresponding member of the French Institute, and a foreign associate of the Reale Accademia dei Lincei, and he shares with his countryman Marignac the honour of being a Davy medallist of the Royal Society. To the great regret of his many friends in England, the illness which ended in his death prevented him from coming to London to receive the medal in person.

He has another association with the memory of Davy, who died at Geneva, which British chemists will not forget. They are grateful to Guye for his pious care of the tomb which holds the remains of the great chemist.

T. E. THORPE.

#### WILLIAM KELLNER.

BORN 1839; DIED SEPTEMBER 12TH, 1922.

WILLIAM KELLNER died at Victoria Road, Charlton, on September 12, in his eighty-third year.

Born at Frankfort in 1839, he received his scientific training under Prof. Wöhler at Gottingen, finally obtaining his Ph.D. degree in that University. He became a Fellow of the Institute of Chemistry in 1878, and served on the Council from 1895 to 1898. In 1862, he came to England as Assistant to Sir H. Roscoe at Owens College, Manchester, whence, in 1864, he went to Woolwich and joined the staff of the War Department Chemist (Sir Frederick Abel, Bart., K.C.B., F.R.S.). In his early years at Woolwich Dr. Kellner was engaged in the varied general work of the Chemical Department, later his main work became investigatory and experimental, both in connexion with explosives, and also to meet the requirements of the various Commissions and Committees on which the War Department Chemist was a prominent member; of these the "Royal Commission on Accidents in Mines" and "The Explosives Com-

mittee" (appointed in 1889 to produce a smokeless powder for the Service) may be mentioned.

Dr. Kellner also devoted much work to the production of an apparatus for the determination of flashing point in oils, and was largely responsible for the Abel flash point apparatus, eventually perfected; in collaboration with Sir Boverton Redwood, he carried out an exhaustive series of tests with this apparatus.

As a scientific worker, Dr. Kellner was painstaking and methodical, displaying much skill in devising experiments to assist in elucidating the various problems confronting him in the course of his work.

As regards practical results, his most important work was in connexion with the evolution of cordite, much of the more difficult research and experimental work leading to the production of this explosive being carried out by Dr. Kellner, in the Chemical Department, at Woolwich Arsenal; in spite of the numerous smokeless powders which have been brought into use since, the fact that after a period of thirty years cordite still remains the British Service propellant for Army and Navy use is perhaps the best testimonial to the thoroughness of his work in this direction.

In 1892 Dr. Kellner succeeded Sir Frederick Abel as Chemist to the War Department, and in addition to the duties of this office served as an Associate Member of the Ordnance Board and as Consulting Chemist to the Royal Gunpowder Factory at Waltham Abbey; he retired from the Service in 1904.

Of an extremely modest and retiring disposition, the value of Dr. Kellner's work was little known outside his Department; he had a kindly and sympathetic nature, and his invariable courtesy and cheerful optimism charmed those he came in contact with; he won the esteem of a large circle of friends.

He was gifted with artistic tastes, a lover of music and devoted to gardening, in his retirement deriving much pleasure from these pursuits. He was unmarried.

O. TRIGGER.

### GEORGE WILLIAM MACDONALD.

DIED AUGUST 7TH, 1922.

To a wide circle of chemists connected for the most part with the explosives industry, the announcement of the death of Mr. George W. MacDonald, O.B.E., M.Sc., brought with it the sense of loss of one with whom was associated the recollection of much pleasant co-operation and friendly intercourse.

Born in Australia of Scottish parents—he claimed to be of the MacDonalds of Glencoe—he was educated in Melbourne and Dunedin

and passed through Melbourne University, taking chemistry under Prof. Orme Masson. Having obtained an 1851 Exhibition Scholarship, he came to England in 1893, and worked at University College with Sir William Ramsay on various subjects, such as the interaction of nitric oxide and sodium ethoxide, the possible occurrence of argon in animal and vegetable substances, the production of cyanides at the temperature of the electric arc, and the disengagement of nitrogen from azides. The last-mentioned process he had frequently carried out with safety, but on completing an operation a few hours after he had heard by cable of the death of his mother, an unfortunate explosion occurred which deprived him of the sight of an eye. Although he recovered the sight of the other eye, its eventual blindness was destined to affect his career.

Undeterred by this experience, after his recovery MacDonald took up the study of explosives in the laboratory of Mr. William Macnab, whence he obtained an appointment with Messrs. Curtis's and Harvey, in the first place in 1896 at their works near Dartford, and later at Cliffe-at-Hoo, where he took charge of the research laboratory in 1908.

MacDonald's work in Curtis's and Harvey's was for the most part concerned with cellulose nitrates, their manufacture and chemical properties. Bringing to bear a mind which was essentially methodical, he determined the conditions and laid down the controls for obtaining consistently the various natures of cellulose nitrate needed for incorporation into blasting explosives, for preparing the firm's smokeless sporting powders, and for making into cordite. He conducted a large body of work on the chemical stability of cellulose nitrate, and was one of the first in this country to introduce, for the purpose of works control, methods for safeguarding the stability of the product, founded on the principle of heating the esters under standard conditions until a marked decomposition supervened. Some of the results of this work on manufacturing processes and on stability were contributed in papers and discussions before the Society of Chemical Industry during the years 1904 to 1914. For many years (1900 to 1916) he contributed to the Journal of that society a series of valuable abstracts from the current literature on explosives.

Always interested in the historical development of his subject, MacDonald brought out in 1912 a book, "Historical Papers on Modern Explosives," in which he described in an interesting manner the work of the discoverers of mercuric fulminate, gunecotton, and nitroglycerine, and the investigations which followed their discovery, describing more minutely the advances made by Abel.

On account of his health, his connexion with Messrs. Curtis's

and Harvey was broken for nearly two years, which he spent in Cairo and in Belguim, where he was engaged in introducing modern plant and processes for a Belgian Company making nitrocellulose.

MacDonald returned, however, to the service of the firm before the war, and took part in designing the subsequent expansion of their works. His keenness to assist was shown at this period by the enthusiasm with which he took up the manufacture of that substitute for cordite (Cordite R.D.B.) which had been put forward from Woolwich as it did not involve the use of acetone. When further extensions of plant for making guncotton were required, his special experience was utilised by the Admiralty in advising on matters of design of plant and of buildings in order to avoid certain dangers.

On the occasion of the recognition of his work at an Investiture of the Order of the British Empire, he received the O.B.E., and had personal consideration at the hands of the King as his eyesight by this time had almost entirely failed. The gradual loss of the sight of his remaining eye, in spite of a series of operations, constituted the tragedy of MacDonald's life, and until near the end the hopefulness and courage with which his friends found him meet his great handicap have always been amongst them a matter for remark and admiration.

It would be wrong at the same time to omit reference to the help which MacDonald had from his wife (*née* Callendar), not only in her care for his health, but also as regards his work. A good linguist, she assisted him in translations from foreign literature, and saved the strain on his eyesight involved by reading and preparation of papers, abstracts, and reports.

On his arrival in England, MacDonald speedily made a large number of friends who were attracted by his personality and the merriness and the sparkling character of his conversation.

Later he will be remembered by the group of chemists who occupied the "explosive table" at the dinners preceding the meetings of the Society of Chemical Industry, as the one who more than any other by his joviality helped to make it justify its name.

Those who knew him will never recall MacDonald without remembering him as one whose characteristic was his willingness to assist either by undertaking work himself or by freely affording the results of his experience, all this being done with a personal charm which was the reason for his circle of friends being both appreciative and large.

He died in London on August 7, 1922.

R. ROBERTSON.



## LIONEL WILLIAM STANSELL.

BORN 1861; DIED MAY 22ND, 1922.

LIONEL WILLIAM STANSELL was born in London in 1861. Educated at the City of London School, he became a pupil of Mr. Otto Hehner in 1877.

After spending eighteen months as assistant to the late C. H. Piesse, he went to Maidstone in 1880 as assistant to the late Dr. M. A. Adams, Public Analyst for the County of Kent, and afterwards became his partner. Dr. Adams retired from practice in 1911 and Stansell acted as County Analyst for two years, until a whole-time appointment was made to that office. Stansell retained, however, the appointments of Public Analyst to the City of Rochester and the Boroughs of Gravesend and Maidstone, and was also engaged in private practice.

Stansell was a conscientious and hard-working analyst, whose whole heart was in his duties. These left him little time for any original work, but in his earlier days he was joint author with Mr. C. H. Piesse of a paper dealing with the analysis of mustard and was also responsible for the chemical work involved in several papers contributed by Dr. Adams to the *Analyst*.

Singularly quiet, modest and reserved, he was little known outside his immediate circle. He was an accomplished musician.

Stansell died, after a long illness, on May 22nd, 1922, leaving a widow and one daughter, his only son having died a few years before as a consequence of war service. He became a Fellow of the Chemical Society in 1887.

E. M. H.

**TRUST DEED ESTABLISHING THE EDWARD  
FRANK HARRISON MEMORIAL FUND.\***

TO ALL ~~TO~~ WHOM these Presents shall come THE CHEMICAL SOCIETY of Burlington House Piccadilly London a Society incorporated by Royal Charter sends greeting :—

WHEREAS in order to create a fund in memory of the late Colonel Edward Frank Harrison deceased formerly Deputy Controller of the Chemical Warfare Department and to commemorate the devoted services he gave in the protection of the British Forces from poison gas in the late Great War a Committee was formed to invite collect and administer subscriptions to the said fund and subscriptions thereto were received from former friends and colleagues of the said Edward Frank Harrison and others amounting in the whole with accrued interest to One thousand six hundred and forty pounds or thereabouts

AND WHEREAS in accordance with the wishes of the subscribers the sum of Five hundred pounds has been expended out of the said fund in the design production and erection of a bronze relief memorial in the rooms of The Chemical Society at Burlington House and in the payment of certain small incidental expenses and the balance of the said fund remaining after payment of certain expenses incidental to the administration of the said fund (including the costs of and incidental to the preparation and execution of these presents) and consisting of Five per cent National War Bonds for One thousand pounds and One hundred and fifty pounds one shilling and five pence cash has by the direction of the said Committee and in accordance with the wishes of the subscribers been transferred to The Chemical Society to be held by it upon the trusts and with and subject to the powers and provisions hereinafter declared

NOW THESE PRESENTS WITNESS and The Chemical Society HEREBY DECLARES as follows :—

1. THE Trust hereby established shall be called "The Edward Frank Harrison Memorial Trust"
2. THE Chemical Society shall either retain the said National War Bonds as invested or at its discretion sell the same or any part thereof and shall invest the proceeds and the said sum of One hundred and fifty pounds one shilling and five pence cash and any other money requiring investment hereunder in any mode of investment from time to time authorised by law for the investment of trust moneys and may at its discretion from time to time vary investments within the prescribed range The investments from time to time representing the said National War Bonds and cash

\* See also Trans., p. 2894.

so transferred to The Chemical Society as aforesaid are hereinafter called "the Fund"

3. THE income of the Fund (including income resulting from the investment of income) or such part thereof as The Chemical Society shall think fit shall be applied in providing periodically and for such selected candidate as hereinafter mentioned a money prize to be called the "Harrison Memorial Prize" not exceeding in each case One hundred and fifty pounds which Prize shall be at the absolute disposal of the recipient free from any restriction. The sum of One hundred pounds cash may be raised out of the corpus of the funds transferred to The Chemical Society and be treated as income of the Fund so as to be available for the provision of the Prize
4. ANY income which in the opinion of The Chemical Society is not required for the provision of the Prize shall be invested so as to form an accretion to the corpus of the Fund with a view to meet the contingency of a reduction in the amount of income from time to time produced by the Fund but if in the opinion of The Chemical Society there is no reasonable probability of the income produced by the Fund being so reduced as to be insufficient to provide the Prize any such surplus income as aforesaid may be applied by The Chemical Society for such purpose having for its object the promotion of Chemical Research as having regard to the objects of the Trust The Chemical Society may think fit
5. The recipient of the Prize shall be selected by a Committee consisting of the Presidents for the time being of The Chemical Society The Institute of Chemistry of Great Britain and Ireland of 30 Russell Square London The Society of Chemical Industry of 46 and 47 Finsbury Square London and The Pharmaceutical Society of 17 Bloomsbury Square London
6. THE President of The Chemical Society shall be Chairman of the Selection Committee and the selection of the recipient of the Prize shall be by a majority vote of the Selection Committee the Chairman in case of equality of votes having a second or casting vote
7. THE Prize shall be awarded to the chemist of either sex being a natural born British subject as for the time being defined by Statute and not at the time over thirty years of age who in the opinion of the Selection Committee shall during the previous five years have conducted the most meritorious and promising original investigations in Chemistry and published the results of those investigations in a scientific periodical or periodicals
8. SUBJECT to the condition that the Selection Committee shall be of opinion that there is a candidate of sufficient distinction to warrant an award of the Prize the first award shall be made in December One thousand nine hundred

and twenty-three and in December of the third year reckoning from and exclusive of each year in which the Prize is in fact awarded the Prize shall subject to the same condition again be awarded. If in any year in which the Prize falls to be awarded the Selection Committee shall be of opinion that there is no such candidate as aforesaid the award of the Prize shall be deferred to the next following year or thereafter from year to year until the Selection Committee shall be of opinion that there is such candidate as aforesaid.

9. UPON every occasion when the Selection Committee shall meet for the purpose of selecting a candidate for the Prize it shall be reminded that the award is not limited to outstanding merit in any special branch of chemistry but that it is to be given for conspicuously meritorious work in any branch of chemistry pure or applied and further that it was intended by those who contributed to the Fund that the Prize should be regarded as an exceptional distinction to commemorate an exceptional man and to be conferred upon the young chemist who in the opinion of those best qualified to judge has made a notable addition to our knowledge of chemistry.
10. THE Officers and Council of The Chemical Society in consultation with the Selection Committee shall decide whether any public announcement of an impending selection of a recipient of the Prize shall be made and if it is to be made shall determine the nature of the announcement.
11. THE Prize shall be presented by the President for the time being of The Chemical Society at an ordinary or special meeting of the Society as soon as possible after the announcement of the award and shall be accompanied by a Certificate or Medal (as shall be hereafter determined by The Chemical Society) to be provided out of the income of the Fund and which Certificate or Medal shall bear the name of him in memory of whom the Fund was founded.

IN WITNESS whereof The Chemical Society has hereunto caused its Common Seal to be affixed the Sixteenth day of November One thousand nine hundred and twenty-two

THE COMMON SEAL of The Chemical Society was hereunto affixed in the presence of

JAMES WALKER, President.  
JOCELYN THORPE, Treasurer.



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**Sulphurous acid**, action of iodine with (MACAULAY), 552.  
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**Thorium**, adsorption of, by basic ferric acetate (BROWN), 1736.  
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**Stannic hydroxide**, amphoteric properties of (COLLINS and WOOD), 441.

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**Titanium salts**, reduction of nitro-paraffins with (HENDERSON and MACBETH), 892.

**Titanous chloride**, action of, on halogen organic compounds (BLACK, HIRST, and MACBETH), 2527.

**Triazo-group** (FORSTER and SAVILLE), 2595.

**Tropic acid**,  $C_9H_{10}O_3$ .

**Tungsten**, reduction of thorium oxide by (GENERAL ELECTRIC Co.), 2236.

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**Uranium-X**, adsorption of, by basic ferric acetate (BROWN), 1736.

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**Valency**, theories of (LAPWORTH), 416; (KERMACK and ROBINSON), 427.

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**Velocity of saponification** of esters (McCOMBIE, SCARBOROUGH, and SKITTLE), 2308.  
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**Xanthorocellin**,  $C_{11}H_{10}O_2N_2$ .

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## FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus  $C_1$  group,  $C_2$  group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

### $C_1$ Group.

$CH_4$  Methane, ignition of mixtures of atmospheric air and (MASON and WHEELER), 2079; synthesis of the polyacetic acids of (INGOLD and PEARREN), 1414; (INGOLD and NICKOLLS), 1638.

$CS_2$  Carbon disulphide, action of, with thallous  $\beta$ -diketones (MORGAN and LEBURY), 2892.

#### I II

$CHN$  Hydrocyanic acid, tautomerism of (USHERWOOD), 1604.

$CH_2O_2$  Formic acid, catalytic decomposition of, on platinum and silver (TINNEY and HINCHELWOOD), 1668; alkali salts, solubility of, in water (SIDGWICK and GENTLE), 1837.

$CH_3O$  Methyl alcohol, equilibrium in the system, water and (PUSHIN and GLAGOLKVA), 2813; purification of, by means of sodium hypochlorite (MENZIES), 2787.

$COCl_2$  Carbonyl chloride, adsorption of, by beechwood charcoal (BUNBURY), 1525.

#### I III

$CHON$  isocyanic acid, condensation of, with aromatic  $\alpha$ -aminosulphonic acids (SCOTT and COHEN), 2034.

$CH_3ONa$  Sodium methoxide, action of, on benzophenone chloride and benzyl idene chloride (MACKENZIE), 1695.

$CH_3ON$  Carbamide, estimation of, with sodium hypobromite (WERNER), 2318.

$CH_3N_2S_2$  Dithiocarbazinic acid, salts, decomposition of (LOSANITCH), 2542.

$CH_3NCl$  Methylammonium chloride, action of dicyanodiamide with (WERNER and BELL), 1790.

$CO_2NCl_2$  Chloropierin, action of, with mercaptans (RAY and DAS), 323.

### $C_2$ Group.

$C_2H_2$  Acetylene, explosion of nitrogen and (GARNER and MATSUNO), 1729.

$C_2H_4$  Ethylene, catalytic hydrogenation of, with nickel (RIDEAL), 809.



## 2 II

- $C_2H_2O_4$  Oxalic acid, lead diphenyl salt (GODDARD, ASHLEY, and EVANS), 981.  
 $C_2H_3O_2$  Acetic acid, alkali salts, solubility of, in water (SIDGWICK and GENTLE), 1837; basic ferric salt, adsorption of radioactive substances by (BROWN), 1736.  
 $C_2H_2N_4$  Dicyanodiamide, action of, with methyl- and dimethyl-ammonium chlorides (WERNER and BELL), 1790.  
 $C_2H_5S_2$  Ethylene mercaptan, reaction of, with mercuric nitrite and ethyl iodide (RAY), 1282.  
 $C_2H_5I$  Ethyl iodide, reactions of, with triethylene tetrasulphide and with ethylene mercaptide nitrite (RAY), 1282.  
 $C_2H_5O$  Ethyl alcohol, solubility of substances in mixtures of water and (WRIGHT), 2251; surface tension of mixtures of water and (BIRCUMSHAW), 887.  
 $C_2H_5N_3$  Methylguanidine, preparation of, and its salts (WERNER and BELL), 1790.  
 $C_2O_2Ru$  Ruthenium carbonyl (MOND and WALLIS), 30.

## 2 III

- $C_2HO_2Cl_3$  Trichloroacetic acid, lead diphenyl salt (GODDARD, ASHLEY, and EVANS), 981.  
 $C_2H_4Cl_2As$   $\beta$ -Chlorovinylchloroarsine (MANN and POPE), 1754.  
 $C_2H_2N_2S_2$  2,5-Dithiol-1:3:4-thiodiazole (LOSANITCH), 2544.  
 $C_2H_4ClS$   $\beta$ -Chloroethyl mercaptan (BENNETT), 2145.  
 $C_2H_4OS$  Thioethyleneglycol, and its metallic mercaptides (BENNETT), 2139.  
 $C_2H_2N_2S_2$  Dithiocarbazinic thioanhydride (LOSANITCH), 2543.  
 $C_2H_4OTl$  Thalliumdimethyl hydroxide, salts of (GODDARD), 37.  
 $C_2H_4NCl$  Dimethylammonium chloride, action of dicyanodiamide with (WERNER and BELL), 1790.

## 2 IV

- $C_2H_5ONBr_2$  Tribromoacetamide (GUPTA and THORPE), 1900.  
 $C_2H_3O_2ClAs$   $\beta$ -Chlorovinylarsinic oxide (MANN and POPE), 1755.  
 $C_2H_3ClSAs$   $\beta$ -Chlorovinylarsenious sulphide (MANN and POPE), 1756.  
 $C_2H_3O_2ClAs$   $\beta$ -Chlorovinylarsinic acid, and its ammonium salt (MANN and POPE), 1755.  
 $C_2H_3O_2ClS$   $\beta$ -Chloroethanesulphonic acid, lead salt (MANN and POPE), 600.  
 $C_2H_3O_2N_2Co$  Diamminodinitro-oxalotocobaltic acid, salts, crystallography, and optical properties of (KNAGGS), 2069.

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- $C_2H_4O$  Acetaldehyde, interaction of aniline and (MANN), 2178.  
 $C_2H_4O$  Acetone, constitution of sugar derivatives of (IRVINE and PATTERSON), 2146.  
 Allyl alcohol, conversion of, into glyceryl bromo- and chloro-hydrins (READ and HURST), 989.  
 $C_2H_3O_2$  Propionic acid, lead diphenyl salt (GODDARD, ASHLEY, and EVANS), 981.  
 $C_2H_3O_2$   $\alpha$ -Trioxymethylene, preparation of (HAMMICK and BOKREE), 2738.  
 $C_2H_3O_2$  Glycerol, equilibrium in the system, water and (PUSHIN and GLAGOLEVA), 2818.  
 $C_2H_5N$  Trimethylamine, hydroferrocyanide of (CUMMING), 1297.  
 $C_2H_5N_3$   $\beta\beta$ -Dimethylguanidine, preparation of, and its salts (WERNER and BELL), 1790.

3 III

- $C_3H_2N_2Br_2$  Dibromoglyoxalines, and their hydrochlorides (BALABAN and PYMAN), 953.  
 $C_3H_2O_2N_2$  Fulminic acid, mercuric salt, velocity of decomposition of (FARMER), 174.  
 $C_3H_2N_2Br$  4-Bromoglyoxaline, and its salts (BALABAN and PYMAN), 951.  
 $C_3H_2OCl_2$  Glyceryl  $\beta$ -dichlorohydrin, preparation of, from allyl alcohol (READ and HURST), 999.  
 $C_3H_2OBr_2$  Glyceryl  $\beta$ -dibromohydrin, preparation of, from allyl alcohol (READ and HURST), 995.  
 $C_3H_2O_2N$  Urethane, equilibrium in the system, *m*-dinitrobenzene and (PUSHIN and FIOLETOVA), 2822.  
 $C_3H_2OCl$  Glyceryl  $\beta$ -monochlorohydrin, preparation of, from allyl alcohol (READ and HURST), 998.  
 $C_3H_2OBr$  Glyceryl  $\beta$ -monobromohydrin, preparation of, from allyl alcohol (READ and HURST), 999.  
 $C_3H_5Br_3Sn$  Tin isopropyl tribromide (DRUCE), 1861.  
 $C_3H_5O_2Sn$  *iso*-Propylstannonic acid, and its salts (DRUCE), 1859.  
 $C_3O_2NCO$  Cobalt nitrosotricarbonyl (MOND and WALLIS), 34.

3 IV

- $C_4HO_2N_2Br_2$  2:4-Dibromo-5-nitroglyoxaline (BALABAN and PYMAN), 958.  
 $C_4HO_2N_2Br$  4-Bromo-5-nitroglyoxaline (BALABAN and PYMAN), 952.  
 $C_4H_2ON_2Br$  Bromocyanosacetamide (GUPTA), 1902.  
 $C_4H_2O_2Cl_2S$   $\beta$ -Dichloropropanesulphonic acid, salts of (POPE and SMITH), 1169.  
 $C_4H_2ON_2S_2$   $\alpha$ -Propanedisulphonyldihydrazide (CLUTTERBUCK and COHEN), 128.

3 V

- $C_4H_2O_2N_2BrS$  4-Bromoglyoxaline-5-sulphonic acid, and its barium salt (BALABAN and PYMAN), 954.

C<sub>4</sub> Group.

- $C_4H_2O_2$  1-Hydroxycyclopropane-1-carboxylic acid (INGOLD, SAKO, and THORPE), 1197.  
 $C_4H_2O_2$  *L*-Malic acid, activation of racemic acid by (MCKENZIE and WALKER), 349.  
 $C_4H_2O_2$  Racemic acid, optical activation of, by *L*-malic acid (MCKENZIE and WALKER), 349.  
 $C_4H_2S$  Divinyl sulphide, synthesis of (BALES and NICKELSON), 2137.  
 $C_4H_2O$  Methyl ethyl ketone, condensation of, in presence of calcium carbide (BECKER and THORPE), 1303.  
 $C_4H_{10}O$  Ethyl ether, properties of mixtures of sulphuric acid, water, and (POUND), 941.  
 $C_4H_{10}O_4$  Erythritol, equilibrium in the system, water and (PUSHIN and GLAGOLEVA), 2820.  
 $C_4H_8S_2$  Dimethyldithiolethylene, reactions of metallic salts with (MORGAN and LEDBURY), 2882.  
 $C_4H_{11}N_2$  *DL*-Alanine-*N*-methylamidine, salts of (PYMAN), 2623.

4 III

- $C_4H_2N_2S_2$  2-Thiol-1:3:4-thiodiazolyl sulphide (LOSANITCH), 2544.  
 $C_4H_2N_2S_2$  2-Thiol-1:3:4-thiodiazolyl disulphide (LOSANITCH), 2545.  
 $C_4H_2N_2S_2$  2-Thiol-1:3:4-thiodiazolyl polysulphide (LOSANITCH), 2545

- $C_3H_5ON$ , 1-Aminocyclopropane-1-carboxylamide, and its hydrochloride (INGOLD, SAKO, and THORPE), 1196.  
 $C_2H_5N_2Br$ , 4:5-Dibromo-2-methylglyoxaline, and its salts (LIGHT and PYMAN), 2627.  
 $C_2H_4Cl_2As$  *ss'*-Dichlorodivinylchloroarsine (MANN and POPE), 1754.  
 $C_2H_5N_2Br$  4-Bromo-2-methylglyoxaline, and its salts (LIGHT and PYMAN), 2628.  
 $C_3H_5O_2N$  1-Aminocyclopropane-1-carboxylic acid, hydrochloride of (INGOLD, SAKO, and THORPE), 1196.  
 $C_2H_4Cl_2S$  *ss'*-Dichlorodiethyl sulphide, preparation and reactions of (MANN and POPE), 594; hydrolysis of, and its non-vesicant isomeride (BALES and NICKELSON), 2137.  
 $C_2H_5N_2S$  Acetonethiosemicarbazone, silver and sodium salts (WILSON and BURNS), 373.  
 $C_2H_5OTl$  Thalliumdiethyl hydroxide, salts of (GODDARD), 37.

## 4 IV

- $C_2H_5O_2N_2Br$ , 2:5-Dibromoglyoxaline-4-carboxylic acid (BALABAN and PYMAN), 956.  
 $C_2H_4ONCl$  Succinchloroimide, preparation of (HIRST and MACBETH), 2174.  
 $C_2H_5O_2N_2Br$  4-Bromo-5-nitro-2-methylglyoxaline (LIGHT and PYMAN), 2629.  
 $C_2H_5O_2Cl_2As$  *ss'*-Dichlorodivinyarsinic acid (MANN and POPE), 1756.  
 $C_2H_4OCl_2S$  *ssss'*-Tetrachlorodiethyl sulphoxide (MANN and POPE), 603.  
 $C_2H_4OCl_2S$  *ssss'*-Trichlorodiethyl sulphoxide (MANN and POPE), 603.  
 $C_2H_5ON_2S$  Thiocarbamide-acetone, picrate of (TAYLOR), 2271.

## 4 V

- $C_2H_5O_2N_2BrS$  4-Bromo-2-methylglyoxaline-5-sulphonic acid ( $+H_2O$ ) (LIGHT and PYMAN), 2629.  
 $C_2H_5O_2N_2BrSCO$  *cis*-Sulphitodiethylenediaminecobaltic bromide ( $+H_2O$ ) (DUFF), 452.  
 $C_2H_5O_2N_2BrS_2CO$  *cis*-Thiosulphatodiethylenediaminecobaltic bromide ( $+3H_2O$ ) (DUFF), 453.  
 $C_2H_5O_2N_2BrSCO$  *cis*-Sulphatodiethylenediaminecobaltic bromide ( $+H_2O$ ) (DUFF), 452.

**C<sub>5</sub> Group.**

- $C_5H_{12}$ , *n*-Pentane, molecular scattering of light in (VENKATESWARAN), 2655.

## 5 II

- $C_5H_5N$  Pyridine, hydroferrocyanide of, and its separation from quinoline (CUMMINS), 1297; isopropylammonium salts of (DRECK), 1861.  
 $C_2H_5N_2$  Dimethylglyoxalines, orientation of (PYMAN), 2616.  
 $C_2H_5N_2$  Aminodimethylglyoxalines, and their salts (PYMAN), 2625.  
 $C_5H_{10}O_2$  Valeric acid, lead diphenyl salt (GODDARD, ASHLEY, and EVANS), 981.  
 $C_5H_{10}O_2$  Xylose, methylation of (CARRUTHERS and HIRST), 2299.  
 $C_5O_5Fe$  Iron pentacarbonyl (MOND and WALLIS), 30.

## 5 III

- $C_5H_8O_2N_2$  5-cycloPropane $\pi$ spirohydantoin (INGOLD, SAKO, and THORPE), 1191.  
 $C_5H_8O_2Cl_2$  Methyl dichloromalonate, preparation of (HIRST and MACBETH), 2177.  
 $C_5H_8O_2N_2$  Ethyl cyanoacetate, condensation of, with ethyl muconate (FARMER), 2015.

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- $C_6H_8O_4N_2$  Nitrodimethylglyoxalines (PYMAN), 2622.  
 $C_6H_8O_4N_2$  1-Nitrosocarbamidocyclopropane-1-carboxylic acid (INGOLD, SAKO, and THORPE), 1195.  
 $C_6H_8O_4Cl$  Methyl chloromalonate, preparation of (HIRST and MACBETH), 2177.  
 $C_6H_8O_4N_2$  1-Carbamidocyclopropane-1-carboxylic acid (INGOLD, SAKO, and THORPE), 1195.  
 $C_6H_{10}NCl$  1-Chloropiperidine, preparation of (HIRST and MACBETH), 2173.  
 $C_6H_{10}O_2N$  Methylaminodimethylacetal (KERMACK, PERKIN, and ROBINSON), 1886.

## 5 IV

- $C_6H_5ONFe$  Nitroprussic acid, carbazole-3-diazonium salts of (MORGAN and READ), 2714.  
 $C_6H_5O_2N_2Br_2$  Bromo-5-cyclopropanespirohydantoin (INGOLD, SAKO, and THORPE), 1191.  
 $C_6H_5O_2ClTe$  Tellurium chloroacetylacetone (MORGAN and DREW), 936.  
 $C_6H_5O_2Cl_2Te$  Tellurium chloroacetylacetone dichloride (MORGAN and DREW), 935.  
 $C_6H_5O_2N_2Br_2$  cyclo Propane-1:1-dicarboxylbromoamide (INGOLD, SAKO, and THORPE), 1190.  
 $C_6H_5O_2N_2Cl_2$  Dichloromalondimethylamide (WEST), 2202.  
 $C_6H_5O_2N_2Br_2$  Dimethylmalonbromoamide (INGOLD, SAKO, and THORPE), 1192.  
 $C_6H_{10}O_2N_2S_2$   $\alpha$ -Pentanedisulphonyldihydrazide (CLUTTERBUCK and COHEN), 128.

## 5 V

- $C_6H_5O_2N_2ClBr$  Chlorobromomalondimethylamide (WEST), 2202.

## C<sub>6</sub> Group.

- $C_6H_6$  Benzene, constitution of (FRASER), 188; variation of the refractive index and density of, with temperature (PARKER and THOMPSON), 1341; action of benzyl chloride and, in presence of iron pyrites (SMYTHE), 1276; chlorination of, with sulphuryl chloride (SILBERRAD), 1015.

## 6 II

- $C_6H_6O$  Phenol, mechanism of the bromination of (BAINES), 2810.  
 $C_6H_4O_2$  Resorcinol, condensation of cinnamic acid with (SHORT and SMITH), 1898.  
 $C_6H_8O_4$  *cis*-3-Methylcyclopropane-1:2-dicarboxylic anhydride (INGOLD), 2687.  
 $C_6H_8O_4$  Muconic acid, constitution of (CHANDRASENA and INGOLD), 1306.  
 $1:2:4:5$ -Tetrahydroxybenzene, colouring matters from (MUKERJI), 545.  
 $C_6H_5N$  Aniline, interaction of acetaldehyde and (MANN), 2178; hydroferrocyanide of (CUMMING), 1293.  
 $C_6H_8O_4$   $\alpha$ -Hydroxy- $\beta$ -methylglutaric lactone, and its salts (INGOLD), 2686.  
 $3$ -Methylcyclopropane-1:2-dicarboxylic acids, and their salts (INGOLD), 2687.  
 $C_6H_8O_4$  *aa*-Dihydroxy- $\beta$ -methylglutaric lactones (INGOLD), 2691.  
 $3$ -Methylcyclopropan-1-ol-1:2-dicarboxylic acid, and its silver salt (INGOLD), 2693.  
 Lactonic acid of butane- $\gamma$ -diol- $\alpha$ -dicarboxylic acid, and its silver salt (INGOLD), 2695.  
 $C_6H_8O_4$  Propane- $\gamma$ -tricarboxylic acid (DICKENS, KON, and THORPE), 1502.

- $C_6H_8N_2$  Phenylenediamine, hydroferrocyanides of (CUMMING), 1295.  
 $C_6H_8O_5$   $\alpha$ -Hydroxy- $\beta$ -methylglutaric acid, and its salts (INGOLD), 2687.  
 $C_6H_{10}O_5$  Methylitamic acid, and its barium salt (INGOLD), 2689.  
 $C_6H_{10}O_5$   $\alpha\alpha'$ -Dihydroxy- $\beta$ -methylglutaric acids, and their salts (INGOLD), 2691.  
 Butane- $\gamma$ -diol- $\alpha\beta$ -dicarboxylic acid, and its salts (INGOLD), 2694.  
 $C_6H_{11}O_5$  Aceritol (PERKIN and UVEDA), 70.  
 $C_6H_{12}O_5$  Fructose, constitution and rotation of compounds of, with boric acid and sodium hydroxide (GILMOUR), 1333.  
 Fructose and Glucose, constitution of acetone derivatives of (IRVINE and PATTERSON), 2146.  
 $C_6H_{12}S_2$  Triethylene trisulphide, and its reactions with mercuric salts, with ethyl iodide, and with platonic chloride (RAY), 1279.  
 $C_6H_{12}S_4$  Triethylene tetrasulphide, and its reactions with mercuric salts and with ethyl iodide (RAY), 1279.  
 $C_6H_{14}O_2$  Pinacone, equilibrium in the system, water and (PUSHIN and GLAGOLEVA), 2816.  
 $C_6H_{14}O_2$  Mannitol, constitution and rotation of compounds of, with boric acid and sodium hydroxide (GILMOUR), 1333.

## 6 III

- $C_6H_3O_7N$  Picric acid, cobaltamine salts of (MORGAN and KING), 1725.  
 $C_6H_3O_7Al$  Aluminioxalic acid, potassium salt, crystallography and optical properties of (KNAGGS), 2072.  
 $C_6H_3O_7Cr$  Chromioxalic acid, potassium salt, autoracemisation of (RIDEAL and THOMAS), 196.  
 $C_6H_3O_7Fe$  Ferrioxalic acid, potassium salt (+  $3H_2O$ ), crystallography and optical properties of (KNAGGS), 2070.  
 $C_6H_3O_7N_3$  1:2:3:4-Benzo-4quinone-1:3-dioxime, cobaltamine and ferric salts of (MORGAN and MOSS), 2857.  
 $m$ -Dinitrobenzene, equilibrium in the system, urethane and (PUSHIN and FIOLETKOVA), 2322.  
 $C_6H_3O_4N_2$  3:5-Dinitrophenol, solubility and volatility of (SIDGWICK and TAYLOR), 1853.  
 $C_6H_5OCl$  Chlorophenols, solubility of (SIDGWICK and TURNER), 2256.  
 $C_6H_5OBr$   $\alpha$ -Bromomuconic acid (CHANDRASENA and INGOLD), 1317.  
 $C_6H_5OBr$   $\alpha$ -Bromo- $\gamma\delta$ -dihydroxy- $\Delta^2$ -dihydromuconic lactone (CHANDRASENA and INGOLD), 1316.  
 $C_6H_5N_2Cl$  Benzenediazonium chloride, interaction of bismuth trichloride and (CHALLENGER and WILKINSON), 102.  
 $C_6H_5OS$   $m$ -Hydroxyphenyl mercaptan (WATSON and DUFF), 2415.  
 $C_6H_8O_4N_2$  2:3:5:6-Tetraketo-1:4-dimethylpiperazine (FORSTER and SAVILLE), 824.  
 $C_6H_8N_2S_2$  2-Thiol-1:3:4-thiodiazolyl sulphide dimethyl ether (LOSASTICH), 2544.  
 $C_6H_8Cl_2As$   $\beta\beta'$ -Trichlorotrivinylarsine, and its salts (MANN and POPE), 1754.  
 $C_6H_5O_2N$   $p$ -Nitrophenylhydrazine, preparation of (DAVIES), 715.  
 $C_6H_7O_2Cl$  Chloro- $\alpha\alpha$ -dimethylsuccinic hydroxyanhydride (FERMER, INGOLD, and THORPE), 158.  
 $C_6H_7O_2Br$  1-Bromo-3-methylcyclopropane-1:2-dicarboxylic acid, and its silver salt (INGOLD), 2632.  
 $C_6H_7O_2Br$  3-Bromo- $\gamma$ -hydroxy- $\Delta^2$ -dihydromuconic acid (CHANDRASENA and INGOLD), 1318.

- $C_4H_8O_2N_2$  *cyclo*Butane*spiro*hydantoin (INGOLD, SAKO, and THORPE), 1192.  
 $C_6H_4O_2Te$  Tellurium 3-methylacetylacetone (MORGAN and DREW), 932.  
 $C_6H_4O_2Br_2$  *aa'*-Dibromo-*β*-methylglutaric acid (INGOLD), 2685.  
 $C_8H_{12}O_4N_2$  *cyclo*Butane-1:1-dicarboxylamide (INGOLD, SAKO, and THORPE), 1191.  
 $C_4H_8Cl_4S$   $\beta\beta'\gamma\gamma'$ -Tetrachlorodipropyl sulphide (POPE and SMITH), 1168.  
 $C_4H_8Cl_4S_2$   $\beta\beta'\gamma\gamma'$ -Tetrachlorodipropyl disulphide (POPE and SMITH), 1169.  
 $C_6H_{11}O_3N$  Ethyl 1-aminocyclopropane-1-carboxylate, hydrochloride (INGOLD, SAKO, and THORPE), 1196.  
 $C_6H_{11}O_2N_2$  *iso*Nitrosomalondimethylamide methyl ether (RENDALL and WHITELEY), 2116.  
 $C_6H_7O_3Sn$  Triformyl derivative of methylstannonic acid (LAMBOURNE), 2639.  
 $C_6H_{11}O_4N$  Glucosamine, mutarotation of, and preparation of its hydrochloride (IRVINE and EARL), 2370.  
 $C_6H_{11}N_2S$  Substance, from ethyl chloroformate and sodium acetoneethiosemicarbazone (WILSON and BURNS), 876.  
 $C_6H_7OSn$  Tin diisopropyl oxide (DUTCE), 1861.  
 $C_6H_7Cl_2Sn$  Tin diisopropyl dichloride (DUTCE), 1862.  
 $C_6H_7Br_2Sn$  Tin diisopropyl dibromide (DUTCE), 1863.  
 $C_6H_{11}O_4N$  Glucamine, production of (LING and NANJI), 1936.  
 $C_6H_{11}O_4N$  Glucose-ammonia, crystalline (LING and NANJI), 1682.  
 $C_6H_{11}SI$  Triethylsulphonium bromide, absorption spectra of, in various solvents (TAYLOR and LEWIS), 665.

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- $C_6H_4O_2Cl_2S$  2:5-Dichlorobenzenesulphonyl chloride (STEWART), 2557.  
 $C_6H_4O_2Na_2$  Silver nitrophenoxides (GODDARD and WARD), 264.  
 $C_6H_4O_2NCs$  Caesium nitrophenoxides (D. and A. E. GODDARD), 56.  
 $C_6H_4O_2NK$  Potassium nitrophenoxides (D. and A. E. GODDARD), 56.  
 $C_6H_4O_2NLi$  Lithium nitrophenoxides (D. and A. E. GODDARD), 56.  
 $C_6H_4O_2NNa$  Sodium nitrophenoxides (D. and A. E. GODDARD), 56.  
 $C_6H_4O_2NRb$  Rubidium nitrophenoxides (D. and A. E. GODDARD), 56.  
 $C_6H_4O_2N_2S$  Dinitrosothioresorcinol (WATSON and DUTT), 1943.  
 $C_6H_4O_2N_2Pb$  Lead 2:4-dinitrophenoxide (GODDARD and WARD), 266.  
 $C_6H_4Cl_2Bi$  *p*-Chlorophenyldibromobismuthine (CHALLENGER and RIDGWAY), 110.  
 $C_6H_4O_2NPb_2$  Lead *o*- and *p*-nitrophenoxides (GODDARD and WARD), 264.  
 $C_6H_4OCl_2As$   $\beta\beta\beta''$ -Trichlorotrivinylarsenic oxide, and its nitrate (MANN and POPE), 1757.  
 $C_6H_4O_2N_2Br_2$  Ethyl 2:5-dibromoglyoxaline-4-carboxylate (BALABAN and PYMAN), 955.  
 $C_6H_4O_2NS$  2-Aminophenol-4-sulphonic acid, cobaltamine salt of (MORGAN and MOSS), 2965.  
 $C_6H_4O_2ClBr$  Methyl  $\gamma$ -chloro- $\beta$ -bromo- $\Delta$ - $\delta$  hydromuconate (CHANDRASENA and INGOLD), 1313.  
 $C_6H_4O_2N_2S$  *p*-Nitroaniline-*o*-sulphonic acid, salts of (SCOTT and COHEN), 2038.  
 $C_6H_4Cl_2Br_2As$   $\beta\beta\beta''$ -Trichlorotrivinylarsine dibromide (MANN and POPE), 1757.  
 $C_6H_4O_2NSe$  Cyano- $\beta$ -selenium acetylacetone (MORGAN, DREW, and BARKER), 2447.  
 $C_6H_4O_2NMg$  Magnesium *m-n* nitrophenoxide (GODDARD and WARD), 264.

- $C_6H_5ONPb$ , Lead *p*-nitrophenoxide (GODDARD and WARD), 265.  
 $C_6H_5O_2N_2S$ , *p*-Nitrophenylhydrazinedisulphonic acid, ammonium salt (DAVIES), 720.  
 $C_4H_8O_2N_2Br$ , *cyclo*Butane-1:1-dicarboxylbromosamide (INGOLD, SAKO, and THORPE), 1191.  
 $C_6H_5O_2Cl_2Te$ , Tellurium 3-methylacetylacetone dichloride (MORGAN and DREW), 931.  
 $C_6H_5O_2Br_2Te$ , Tellurium 3-methylacetylacetone dibromide (MORGAN and DREW), 932.  
 $C_6H_5O_2I_2Te$ , Tellurium 3-methylacetylacetone diiodide (MORGAN and DREW), 932.  
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 $C_7H_7Cl_3IAs$  66'8"-Trichlorotrivinylmethylarsonium iodide (MANN and LOPE), 1758.  
 $C_7H_{10}O_2Cl_2Te$  Tellurium 3-ethylacetylacetone dichloride (MORGAN and DREW), 932.  
 $C_7H_{10}O_2Br_2Te$  Tellurium 3-ethylacetylacetone dibromide (MORGAN and DREW), 934.  
 $C_7H_{10}O_2I_2Te$  Tellurium 3-ethylacetylacetone diiodide (MORGAN and DREW), 934.  
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 $C_6H_5O_2Cl$  2-Chloro-5:5-dimethyldicyclopentan-3-one-1-carboxylic acid (FARMER, INGOLD, and THORPE), 154.  
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 $C_6H_5OBr$  Methyl- $\alpha$ -bromomucconate (CHANDRASENA and INGOLD), 1317.  
 $C_6H_5ON_2$   $p$ -Nitrosodimethylaniline, hydroferrocyanide of (CUMMING), 1297.  
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 $C_6H_5ON$  8-Benzylsemicarbazide, and its hydrochloride (WILSON, HOPPER, and CRAWFORD), 863.  
 $C_6H_5O_2Cl$  Chlorodimethyldihydroresorcinol, action of phosphorus chlorides on (HINKEL and WILLIAMS), 2493.  
 $C_6H_5O_2Br$  Bromo-5:5-dimethyldicyclopentan-3-one-2-carboxylic acids (FARMER, INGOLD, and THORPE), 158.

- $C_6H_{11}N_2S$  *S*-Benzylthiosemicarbazone, salts of (WILSON and BUGINS), 874.  
 $C_6H_5ON_2$  *m*-Methoxyphenylmethylhydrazine; preparation of (KERMACK, PERKIN, and ROBINSON), 1880.  
 $C_6H_5O_2Br_2$  Methyl  $\alpha\alpha'$ -dibromo- $\beta$ -methylglutarate (INGOLD), 2686.  
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 $C_6H_5O_2Sn_4$  Pentaformyl derivative of methylataannonic acid (LAMBOURNE), 2538.  
 $C_6H_5O_2N_2$  *iso*-Nitrosomalondimethylamide *n*- and *iso*-propyl ethers (RENDALL and WHITLEY), 2117.  
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 $C_6H_4O_2NCl$  Chloroconmaran-2-one oximes (MINTON and STEPHEN), 1602.  
 $C_6H_4O_2NCl$  Nitrophenoxyacetyl chlorides (MINTON and STEPHEN), 1593.  
 $C_6H_4ONCl_2$   $\omega$ -Dichlorotoluamides (DAVIES and PERKIN), 2211.  
 $C_6H_4O_2NCl$  Chlorophenoxyacetamides (MINTON and STEPHEN), 1601.  
 $C_6H_4O_2N_2S$  Substance, from *p*-carbamidotoluene-*m*-sulphonic acid and phosphoryl chloride (SCOTT and COHEN), 2041.  
 $C_6H_4ON_2S$  Thiocarbamide-benzaldehyde, picrate of (TAYLOR), 2269.  
 $C_6H_4O_2N_2S$  Thiocarbamide-salicylaldehyde, picrate of (TAYLOR), 2269.  
 $C_6H_4O_2N_2S$  *p*-Carbamidotoluene-*m*-sulphonic acid, and its salts (SCOTT and COHEN), 2039.  
 $C_6H_4O_2N_2S$  *N*-*m*-Nitrophenyl- $\beta$ -aminoethyl hydrogen sulphate, and its nitroaniline salt (SAUNDERS), 2674.  
 $C_6H_4O_2NS$  *N*-Phenyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2671.

## 8 V

- $C_6H_4O_2N_2ClS$  *p*-Chlorophenylbiuret-*o*-sulphonic acid, potassium salt (+2H<sub>2</sub>O) (SCOTT and COHEN), 2048.  
 $C_6H_4O_2N_2BrS$  *p*-Bromophenylbiuret-*o*-sulphonic acid, and its salts (SCOTT and COHEN), 2045.  
 $C_6H_4O_2N_2IS$  *p*-Iodophenylbiuret-*o*-sulphonic acid, and its salts (SCOTT and COHEN), 2049.  
 $C_6H_4O_2NClS$  *N*-*p*-Chlorophenyl- $\beta$ -aminosthyl hydrogen sulphate (SAUNDERS), 2675.

## C, Group.

- $C_9H_8$  Indene, action of bromine water on (READ and HURST), 2550.

## 9 II

- $C_9H_7N$  *iso*Quinoline (HARRIS and POPE), 1029.  
 Quinoline, separation from pyridine and hydroferrocyanides of (CUMMING), 1298.  
 $C_9H_7O_2$  Cinnamic acid, condensation of resorcinol and (SHORT and SMITH), 1808.  
 $C_9H_7O_2$  Methyl aldehydosalicylates, and their sodium salts (WAYNE and COHEN), 1022.  
 $C_9H_7O_2$  Methanetetra-acetic anhydride (INGOLD and NICKOLLS), 1647.

- $C_7H_{10}O_2$  'Homopiperonyl methyl ether (GREENE and ROBINSON), 2194.  
Tropic acid, resolution of, and its salts (KING and PALMER), 2677.
- $C_8H_{10}O_4$  1-Hydroxycyclopentylethane- $\alpha\beta$ -dicarboxylic lactone (BIRCH and THORPE), 1836.
- $C_8H_{12}O_4$   $\Delta^2$ -Butene- $\alpha\beta$ -dicarboxylic- $\beta$ -malonic acid, sodium salt (FARMER), 2020.
- $C_8H_{10}N_2$  Dinitrile of cyclopentanespirocyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1834.
- $C_8H_{12}O_4$  cycloPentanespirocyclopentane-3:4-dione (KON), 526.
- $C_8H_{12}O_5$  Castelagenin (BORMAN), 971.  
Anhydride of *cis*-3:3-diethylcyclopropane-1:2 dicarboxylic acid (DESHAPANDE and THORPE), 1437.
- $C_8H_{12}O_6$  Trimethyltricarballic anhydride (HOPZ and SHELDON), 2235.
- $C_8H_{12}O_8$  Methanetetra-acetic acid, and its salts (INGOLD and NICKOLLS), 1646.  
*iso*Pentane- $\alpha\beta\beta\beta$ -tetracarboxylic acid (INGOLD and NICKOLLS), 1647.
- $C_8H_{12}N_2$  Dinitrile of 1:1-diethylcyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1826.
- $C_8H_{14}O$  cycloHexanespirocyclobutan-3-one (KON), 520.  
4-*iso*Propylidenecyclohexanone, reduction of (HENDERSON, ROBERTSON, and BROWN), 2721.
- $C_8H_{14}O_4$   $\alpha$ -Campholytic acid, intra-annular tautomerism of (CHANDRASENA, INGOLD, and THORPE), 1542.  
1:1-Diethylcyclopentane-3:4-dione (DICKENS, KON, and THORPE), 1506.
- $C_8H_{14}O_5$  Ethyl 3-methylcyclobutan-1-one-3-acetate (INGOLD), 1151.
- $C_8H_{14}O_5$  *d*-3-Carboxy-1:1-dimethylcyclopropane-2-propionic acid, and its copper salt (SIMONSEN), 2297.  
1-Carboxycyclohexyl-1-acetic acid (LAWWORTH and McRAE), 2754.  
*cis*- and *trans*-3:3-Diethylcyclopropane-1:2-dicarboxylic acids (DESHAPANDE and THORPE), 1437.  
Ethyl ethyldienemalonate, preparation of  $\gamma$ -alkylidene derivatives of (HIGGINBOTHAM and LAWORTH), 2823.  
Homoterpenylic acid, preparation of (SIMONSEN), 2298.
- $C_8H_{14}O_5$  3:3-Diethylcyclopropanol-1:2-dicarboxylic acid (DESHAPANDE and THORPE), 1440.  
5:5-Dimethylcyclopentan-3-ol-1:2-dicarboxylic acid (FARMER, INGOLD, and THORPE), 152.  
Hydroxy-lactonic acid, from hydrolysis of ethyl  $\alpha\alpha'$ -dibromo- $\beta\beta$ -diethylglutarate (DESHAPANDE and THORPE), 1438.  
 $\beta$ -Keto- $\beta$ -carboxy- $\gamma\gamma$ -dimethylhexoic acid (CHANDRASENA, INGOLD, and THORPE), 1549.  
 $\alpha$ -Keto- $\beta\beta$ -diethylglutaric acid, and its calcium salt (DESHAPANDE and THORPE), 1439.
- $C_8H_{12}O_6$  Substance, from oxidation of trimethyl glucose (HAWORTH and LEITCH), 1929.
- $C_8H_{12}O_6$  Azelaic acid, electro-synthesis of (CARMICHAEL), 2545.  
 $\gamma\delta$ -Dihydroxydihydro- $\alpha$ -campholytic acid (CHANDRASENA, INGOLD, and THORPE), 1548.  
 $\alpha$ -Ethyl- $\beta\beta$ -dimethylglutaric acid (KON and THORPE), 1800.
- $C_8H_{12}O_6$  Nonoic acid, sodium salt, properties of solutions of (FLECKER and TAYLOR), 1101.
- $C_8H_{12}O_6$  Trimethyl methylxyloside, preparation of (CARRUTHERS and HIRST), 2304.
- $C_8H_{12}O_6$  2:3:6-Trimethylglucose (IRVINE and HIRST), 1218.
- $C_8H_{12}O_6$  2:3:6-Trimethyl methylglucoside (IRVINE and HIRST), 1222.

## 9 III

- $C_8H_6O_2N_2$  Nitrocinnamonnitriles (BRADY and THOMAS), 2107.  
 $C_8H_6O_2Hg$  4:5-Anhydro-3-acetoxymercuri-5-hydroxymercuri-4-hydroxybenzaldehyde (HENRY and SHARP), 1058.  
 $C_8H_6O_2N_2$  Methyl dinitro-5-aldehydosalicylate (WAYNE and COHEN), 1025.  
 $C_8H_6O_2Cl_3$  Methyl  $\alpha$ -trichlorotoluates (DAVIES and PERKIN), 2213.  
 $C_8H_6O_2Br$  Methyl 5-bromoaldehydosalicylate (WAYNE and COHEN), 1024.  
 $C_8H_6O_2N$  Methyl 5-nitroaldehydosalicylate (WAYNE and COHEN), 1024.  
 $C_8H_6O_2N_2$  Nitrocinnamonaldoximes (BRADY and THOMAS), 2107.  
 $C_8H_6O_2S_2$  2-Carboxyphenyldithioglycollic acid (SMILES and McCLELLAND), 88.  
 $C_8H_6O_2Hg$  Acetoxymercuri-m-hydroxybenzaldehyde (HENRY and SHARP), 1059.  
 $C_8H_6ON$  Cinnamaldoximes (BRADY and THOMAS), 2098.  
 $\delta$ -Methoxyindole, and its picrate (KERNACK, PERKIN, and ROBINSON), 1879.  
 $C_8H_6OBr$  Indene bromohydrin (READ and HURST), 2552.  
 Bromohydroxyhydrindene (READ and HURST), 2554.  
 $C_8H_6O_2N_2$   $\alpha$ -Triazo- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid (FORSTER and SAVILLE), 2600.  
 $C_8H_6O_2Cl$  Cinnamic acid chlorohydrin, preparation and reactions of (FORSTER and SAVILLE), 2595.  
 $C_8H_6O_2N$  Methyl 5-aldehydosalicylate oxime (WAYNE and COHEN), 1026.  
 $C_8H_6O_2N$  Methyl nitrophenoxacetates (MINTON and STEPHEN), 1593.  
 $\delta$ -Nitrohomopiperonyl methyl ether (GREENE and ROBINSON), 2194.  
 Nitrotoloxycetic acids (MINTON and STEPHEN), 1594.  
 $C_8H_6O_2N_2$  Dinitroaceto-*m*-toluidides (BRADY, DAY, and ROLT), 532.  
 Dinitroaceto-*p*-toluidides (SCOTT and ROBINSON), 845.  
 $C_8H_6O_2N_2$  Nitroaceto-*m*-toluidides (BRADY, DAY, and ROLT), 529.  
 $C_8H_6O_2N_2$  3-Carbamido-4-methoxybenzoic acid (FROELICHER and COHEN), 1656.  
 Nitrotoloxycetamides (MINTON and STEPHEN), 1595.  
 $C_8H_{11}OCl$  Benzyl  $\beta$ -chloroethyl ether (CLEMO and PERKIN), 649.  
 $C_8H_{11}ON$  *L*-Atrolactinamide, preparation and rotation of (McKENZIE and SMITH), 1356.  
 $C_8H_{11}O_2N_2$  *p*-Nitrobenzaldehydedimethylhydrazone, and its hydrochloride (BRADY and McHUGH), 1651.  
 $C_8H_{11}O_2N$  Aminotoloxycetic acids (MINTON and STEPHEN), 1597.  
 $C_8H_{11}NCl$   $\beta$ -Chloroethylmethylaniline (CLEMO and PERKIN), 648.  
 $C_8H_{11}ON_2$   $\delta$ - $\alpha$ -Phenylethylsemicarbazides, and their hydrochlorides (WILSON, HOPPER, and CRAWFORD), 869.  
 $C_8H_{11}O_2N_2$  Substance, from hydrolysis of ethyl  $\beta$ - $\gamma$ -dicyano- $\gamma$ -methylbutane- $\beta$ -dicarboxylate (HOPE and SHELTON), 2232.  
 $C_8H_{12}O_2Cl$  Ethyl  $\beta$ -chloroglutaconate (INGOLD and NICKOLLS), 1643.  
 $C_8H_{12}O_2Br_2$   $\alpha\alpha'$ -Dibromo- $\beta\beta$ -diethylglutaric acid (DESHAPANDE and THORPE), 1436.  
 $C_8H_{12}O_2N_2$  1:1-Dimethyl- $\gamma$ -lopentane-3:4-dione disemicarbazone (KON), 524.  
 $C_8H_{12}O_2N_2$  Heptaldehydesemioxamazone (LAPWORTH and McRAE), 2753.  
 $C_8H_{12}O_2N_2$   $\alpha\alpha$ -Nitrosomalondimethylamide *n*-butyl ether (RENDALL and WHITELEY), 2117.  
 $C_8H_{12}O_2Sn$  Triacetyl derivative of methylstannonic acid (LAMBOURNE), 2537.

# FORMULA INDEX.

9 III-10 II

- $C_6H_{11}O_4N$  Trimethyl glucosioxime (IRVINE and HIRST), 1220.  
 $C_6H_{11}O_4N$  Methylaminobisdimethylacetal (KERMACK, PERKIN, and ROBINSON), 1886.

## 9 IV

- $C_6H_3O_4N_2Cl_2$  Mesoxalic acid 2:4-dichlorophenylhydrazones (CHATTAWAY and HARRIS), 2708.  
 $C_6H_3O_4N_2Br_2$  Mesoxalic acid 2:4-dibromophenylhydrazones (CHATTAWAY and HARRIS), 2709.  
 $C_6H_3O_4N_2Cl$  Mesoxalic acid chlorophenylhydrazones (CHATTAWAY and HARRIS), 2708.  
 $C_6H_3O_4N_2Br$  Mesoxalic acid *p*-bromophenylhydrazones (CHATTAWAY and HARRIS), 2708.  
 $C_6H_4N_2Cl_2S$  Substance, from *p*-chlorophenylthiocarbamide and chloropierin (RAY and DAS), 326.  
 $C_6H_3O_4N_2Cl$  Semicarbazones of chlorocoumaran-2-ones (MINTON and STEPHEN), 1602.  
 $C_6H_3O_4N_2Cl_2$  2:6-Dichloro-3-nitroaceto-*p*-toluidide (DAVIES), 813.  
 $C_6H_3O_4NCl$  Nitrotoloxylacetyl chlorides (MINTON and STEPHEN), 1594.  
 $C_6H_3ONCl_2$  Acetyl derivative of 2:6-dichloro-*p*-toluidine (DAVIES), 813.  
 $C_6H_3ONI$  Acetyl derivative of 6-iodo-*m*-toluidine (BRETTON and KENNER), 680.  
 $C_6H_9O_4N_2Cl$  *p*-Nitro-*o*-tolyl  $\beta$ -chloroethyl ether (CLEMO and PERKIN), 645.  
 $C_6H_9O_4N_2S$  *o*-Acetylcarbamidobenzenesulphonic acid, potassium salt (+  $H_2O$ ) (SCOTT and COHEN), 2042.  
 $C_6H_8N_2S$  Benzothiazole ethiodide (MILLS), 460.  
 $C_6H_9O_4Cl_2S$   $\beta$ -Chloroethyl toluene-*p*-sulphonate (CLEMO and PERKIN), 644.  
 $C_6H_{11}ON_2S$  Thiocarbamideacetone, picrate of (TAYLOR), 2272.  
 $C_6H_9O_4NS$  *N*-Phenyl-*N*-methyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2674.  
*N*-*o*-Tolyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2673.

## 9 V

- $C_6H_9O_4N_2BrS$  Acetyl-*p*-bromophenylcarbamide-*o*-sulphonic acid, potassium salt (SCOTT and COHEN), 2047.

## $C_{10}$ Group.

- $C_{10}H_{12}$  Tetrahydronaphthalene, preparation of derivatives of (STEVENSON and THORPE), 1717.  
 $C_{10}H_{16}$  Sabinene, oxidation of, with chromyl chloride (HENDERSON, ROBERTSON, and BROWN), 2717.

## 10 II

- $C_{10}H_8O_4$  2:4-Dicarboxycyclobutane-1:3-diacetic anhydride (INGOLD, PEBEREN, and THORPE), 1789.  
 $C_{10}H_8O_4$  Hydroxycarboxycinnamic acids (WAYNE and COHEN), 1028.  
 $C_{10}H_8N_2$   $\alpha$ - and  $\beta$ -Naphthylamines, hydroferrocyanides of (CUMMING), 1295.  
 $C_{10}H_{12}O_2$  *o*- and *p*-Hydroxystyryl methyl ketones (BROCK and HEILBRON), 1100.  
 $C_{10}H_{12}O_4$  Methyl 2-methoxy-5-aldehydobenzoate (WAYNE and COHEN), 1023.  
Phenylsuccinic acid, preparation of (LAWFORTH and McRAE), 1704.  
 $C_{10}H_{11}N$  5:8-Dihydro- $\alpha$ -naphthylamine, oxidation and bromination of (ROWE and DAVIES), 1000.  
 $C_{10}H_{14}O$  Cuminaldehyde, from eucalyptus oil (PENFOLD), 266.

- $C_{12}H_{18}O_6$  1-Hydroxycyclopentylethane- $\alpha\alpha\beta$ -tricarboxylic lactone (BIRCH and THORPE), 1835.
- $C_{12}H_{18}O_6$  2:4-Dicarboxycyclobutane-1:3-diacetic acids (INGOLD, PERREN, and THORPE), 1789.
- $C_{12}H_{18}O_6$  *cyclo*Hexanespirocyclopentane-3:4-dione (KON), 522.
- $C_{12}H_{18}O_6$   $\alpha$ -Keto- $\alpha$ -campholenic acid (CHANDRASENA and INGOLD), 1554.
- $C_{12}H_{18}O_6$  Ethyl muconate, addition of ethyl sodiocyanacetate and ethyl sodio-malonate to (FARMER), 2015.
- $C_{12}H_{18}O_6$   $\gamma$ -Hydroxy- $\gamma$ -ethylpentane- $\alpha\alpha\beta$ -tricarboxylic lactone (BIRCH and THORPE), 1826.
- $C_{12}H_{18}O$  Cryptal, from eucalyptus oil (PENFOLD), 266.
- Phellandral, from eucalyptus oil (PENFOLD), 266.
- Piperitone (READ and SMITH), 574, 1863; (READ, SMITH, and BENTIVOGLIO), 582.
- Sabinenilanaldehyde (HENDERSON, ROBERTSON, and BROWN), 2720.
- $C_{12}H_{18}O_2$  1:4-Dimethyl-1-ethylcyclohexane-3:5-dione (BECKER and THORPE), 1305.
- Sabinenilanic acid, and its salts (HENDERSON, ROBERTSON, and BROWN), 2720.
- $C_{12}H_{18}O_2$  *d*-1:1-Dimethyl-2- $\gamma$ -ketobutylcyclopropane-3-carboxylic acid, and its sodium salt (SIMONSEN), 2295.
- $C_{12}H_{18}O_2$  Ethyl *n*-heptenecarboxylate (CARMICHAEL), 2549.
- $C_{12}H_{18}O_2$  Methyl  $\beta$ -methyl- $\beta$ -ethylglutarate (DICKENS, KON, and THORPE), 1503.
- $C_{12}H_{18}O_2$  Ethyl butane- $\alpha\gamma$ -diol- $\alpha\beta$ -dicarboxylate (INGOLD), 2694.
- $C_{12}H_{18}O_2$   $\alpha\alpha'$ -Dimethyldisobutenyl disulphide (POPE and SMITH), 1168.
- $C_{12}H_{18}O_2$  1:3:4:6-Tetramethyl fructose (IRVINE and PATTERSON), 2697.
- Trimethyl methylglucoside (HAWORTH and LEITCH), 1928.

## 10 III

- $C_{12}H_9O_2N_2$  2:4-Dinitro- $\alpha$ -naphthol, cobaltammine salts of (MORGAN and KING), 1727.
- $C_{12}H_9OS$  Hydroxynaphthyl mercaptans (WATSON and DUTT), 2416.
- $C_{12}H_9O_2N_2$  2:6-Dihydroxy-*m*- $\alpha$ -benzobispyrrole, and its sodium salt (DAVIES and HICKOX), 2652.
- $C_{12}H_9O_2N_2$  4:6-Dinitrophenylene-1:3-diacetic acid, and its lead salt (DAVIES and HICKOX), 2651.
- $C_{12}H_9N_2S_2$  Dimethylbenzbisthiazoles, and their salts (EDGE), 774.
- $C_{12}H_9ON$  6-Methoxyindole-3-aldehyde (KERMACK, PERKIN, and ROBINSON), 1882.
- $C_{12}H_9O_2Cl$  3-Chlorobenzoylacetone (MORGAN, DREW, and BARKER), 2456.
- $C_{12}H_9O_2N$  Methyl 6-nitropiperonylacetate (GREENE and ROBINSON), 2195.
- $C_{12}H_9O_2N_2$  *cyclo*Pentanespiro-2:3-dicyanocyclopropane-2-carboxylic acid (BIRCH and THORPE), 1834.
- Phenylcyanourethane (SCOTT and COHEN), 2050.
- $C_{12}H_{11}O_2Cl_2$  Ethyl  $\alpha$ -dichlorotoluates (DAVIES and PERKIN), 2211.
- $C_{12}H_{11}O_2N_2$  Mesoxalic acid tolylhydrazones (CHATTAWAY and HARRIS), 2709.
- $C_{12}H_{11}ON_2$  *cyclo*Pentanespiro-2:3-dicyanocyclopropane-2-carboxylamide (BIRCH and THORPE), 1834.
- $C_{12}H_{11}O_2Br$  Ethyl  $\alpha$ -bromo-*o*-toluate (DAVIES and PERKIN), 2207.
- $C_{12}H_{11}O_2I$  Ethyl  $\alpha$ -iodo-*o*-toluate (DAVIES and PERKIN), 2208.

- $C_{15}H_{11}O_2N_2$  Acetyl-*p*-nitrobenzaldehydemethylhydrazone (BRADY and McHUON), 1652.
- $C_{15}H_{11}O_2N_2$   $\alpha$ -Triazo- $\beta$ -methoxy- $\beta$ -phenylpropionic acid (FORSTER and SAVILLE), 2601.
- $C_{15}H_{11}O_4N_2$  Semicarbazone of methyl 5-aldehydosalicylate (WAYNE and COHEN), 1026.
- $C_{15}H_{11}O_4N$  Ethyl nitrophenoxyacetates (MINTON and STEPHEN), 1593.
- Methyl nitrotololyoxyacetates (MINTON and STEPHEN), 1594.
- $C_{15}H_{12}ON_2$  2:3-Dicyano-1:1-diethylcyclopropane-2-carboxylamide (BIRCH and THORPE), 1825.
- $C_{15}H_{12}O_2N_2$  2:3-Dicyano-1:1-diethylcyclopropane-2-carboxylic acid (BIRCH and THORPE), 1825.
- $C_{15}H_{12}O_2N$   $\alpha$ -1:1-Dimethyl-2- $\gamma$ -ketobutylcyclopropane-3-carboxylic acid oxime (SIMONSEN), 2296.
- $C_{15}H_{12}O_4Se$  Selenium *OC*-bisacetylacetone (MORGAN, DREW, and BARKER), 2449.
- $C_{15}H_{12}O_4Se_2$  Diselenium bisacetylacetone (MORGAN, DREW, and BARKER), 2444.
- $C_{15}H_{12}OBr$   $\alpha$ -Bromocamphor (LOWRY, STEELE, and HURGESS), 633.
- $C_{15}H_{12}O_2Br$  Ethyl  $\gamma$ -bromoacetylsuccinate, preparation of (HIRST and MACBETH), 2175.
- $C_{15}H_{12}O_2Br_2$  Ethyl  $\alpha\alpha'$ -dibromo- $\beta$ -methylglutarate (INGOLD), 2686.
- $C_{15}H_{12}O_2Br_2$  Ethyl  $\alpha\beta$ -dibromo- $\gamma\delta$ -dihydroxyadipate (CHANDRASENA and INGOLD), 1316.
- $C_{15}H_{17}ON$  *dl*-Piperitons oximes, and their hydrochlorides (READ, SMITH, and BENTIVOGLIO), 582.
- $C_{15}H_{17}ON_2$  *cyclo*Hexanespirocyclobutan-3-one semicarbazone (KON), 520.
- $C_{15}H_{17}O_2N$   $\alpha$ -Hexylsuccinimide (LAPWORTH and McRAE), 2750.
- $C_{15}H_{17}OI$  Ethyl  $\alpha$ -iodo- $\beta$ -methylglutarate (INGOLD), 2685.
- $C_{15}H_{17}O_2N$  Semicarbazone of  $\alpha$ -keto- $\beta\beta$ -diethylglutaric acid (DESHA-PANDE and THORPE), 1440.
- $C_{15}H_{17}O_2N_2$  Disemicarbazone of 1-methyl-1-ethylcyclopentane-3:4-dione (DICKENS, KON, and THORPE), 1504.
- $C_{15}H_{17}O_2N$  Hexylsuccinamic acid (HIGGINBOTHAM and LAPWORTH), 52.
- $C_{15}H_{16}Cl_2S_2$   $\beta\beta'$ -Dichloro- $\alpha\alpha'$ -dimethyldiisobutyl disulphide (POPE and SMITH), 1167.

10 IV

- $C_{16}H_{12}O_2N_2S$  2:4-Dinitro- $\alpha$ -naphthol-7-sulphonic acid, cobaltammine salts of (MORGAN and KING), 1727.
- $C_{16}H_{12}O_2N_2S_2$  Dinitrodithioacetacetanilide (NAIK and AVASARE), 2594.
- $C_{16}H_{12}O_2NS_2$  8-Amino- $\alpha$ -naphthol-3:6-disulphonic acid, cobaltammine salt (MORGAN and MOSS), 2864.
- $C_{16}H_{12}ONCl$  3-Chloro-7-methoxyquinoline (KERMACK, PERKIN, and ROBINSON), 1888.
- $C_{16}H_{12}O_2NS_2$  Dithioacetacetacetanilide (NAIK and AVASARE), 2594.
- $C_{16}H_{12}O_2NCl$  *p*-Chloroacetylaminophenyl chloroacetate (BARNETT and COOK), 765.
- $C_{16}H_{12}O_2N_2BrS$  Acetyl-*p*-bromophenylbiuret- $\alpha$ -sulphonic acid, potassium salt (SCOTT and COHEN), 2046.
- $C_{16}H_{12}ON_2S$  Thiocarbamidcinnamaldehyde, and its salts (TAYLOR), 2270.
- $C_{16}H_{12}O_2NCl$  Acetylaminophenyl- $\beta$ -chloroethyl ethers (CLEMO and PERKIN), 645.



- $C_{10}H_9O_4N_2S_2$  Substance, from 2-thiol-4:5-dihydrothiazole and chloropicrin (RAY and DAS), 325.  
 $C_{10}H_9O_4Cl_2Te$  Tellurium bischloroacetylacetone dichloride (MORGAN and DREW), 938.  
 $C_{10}H_{12}O_4Se_2Cu$  Copper diselenium bisacetylacetone (MORGAN, DREW, and BARKER), 2447.  
 $C_{10}H_{13}O_4N_2S$  *p*-Acetylcarbamidotoluene-*m*-sulphonic acid, potassium salt (SCOTT and COHEN), 2040.  
 $C_{10}H_7NIS$  Methylbenzothiazole ethiodides (MILLS), 460; (MILLS and BRAUNHOLTZ), 1493.  
 $C_{10}H_7ON_2S$  Phenylthiocarbamideacetone, picrate of (TAYLOR), 2272.  
 $C_{10}H_9O_4Cl_2Te$  Tellurium bisacetylacetone dichloride (MORGAN and DREW), 929.  
 $C_{10}H_{11}O_4N_2S$  *N-p*-Nitroso-*N*-ethyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2674.  
 $C_{10}H_{11}O_4NS$  Methylethylsulphine-*p*-toluenesulphonylimine (MAAN and POPE), 1053.  
 $C_{10}H_{11}O_4NS$  *N*-Phenyl-*N*-ethyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2673.  
 $C_{10}H_9O_4Cl_2Te$  Tellurium *O*-ethylpivalylacetone trichloride (MORGAN and DREW), 938.

### $C_{11}$ Group.

- $C_{11}H_{16}O_6$  Acetyl derivative of methyl 5-aldehydosalicylate (WAYNE and COHEN), 1022.  
 $C_{11}H_{18}O_6$  Piperonylsuccinic acid (LAPWORTH and McRAE), 1707.  
 $C_{11}H_{18}O_6$   $\alpha$ -Methylcyclohexane-1:1-diacetic anhydride (KON and THORPE), 1801.  
 $C_{11}H_{16}N_4$  Benzaldehydediethylhydrazone, and its platinumchloride (BRADY and McHUGH), 1850.  
 $C_{11}H_{18}O_6$   $\alpha$ -Methylcyclohexane-1:1-diacetic acid (KON and THORPE), 1801.  
 Methylcyclopentane-1:1-diacetate (DICKENS, KON, and THORPE), 1502.  
 $C_{11}H_{18}O_6$  Ethylester of hydroxy-lactonic acid,  $C_6H_{11}O_5$  (DESHAPANDE and THORPE), 1433.  
 $C_{11}H_{20}O_4$  Methyl  $\beta$ : $\beta$ -diethylglutarate (DICKENS, KON, and THORPE), 1504.

### II III

- $C_{11}H_9ON$  Nitro-2-hydroxy- $\alpha$ -naphthaldehyde (MORGAN and REEVES), 6.  
 $C_{11}H_7NS$   $\alpha$ -Naphthyl thiocyanate (CHALLENGER and WILKINSON), 100.  
 $C_{11}H_{13}O_4N$  Quinaldinic acid methyl betaine (MILLS and HAMER), 2011.  
 $C_{11}H_9O_4N$  Imide of cyclopentanecyclo-2:3-dicyanocyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1831.  
 $C_{11}H_{13}O_4N$  6-Amino-2-hydroxy-3-naphthoic acid (FROELICHER and COHEN), 1659.  
 $C_{11}H_{13}ON$   $\alpha$ -Cyano- $\gamma$ -phenylcrotonamide (STEVENSON and THORPE), 1720.  
 $C_{11}H_{13}O_4N$  Substance, from  $\alpha$ -ketoglutaric acid and *o*-phenylenediamine (KON, STEVENSON, and THORPE), 664.  
 $C_{11}H_{13}O_4N$  *m*-Acetylamino-phenoxyacetic acid (MIXON and STEPHEN), 1597.  
 $C_{11}H_{13}O_4N$  Acetylcinnamonaldoximes (BRADY and THOMAS), 2197.  
 $C_{11}H_{13}O_4N$   $\alpha$ : $\beta$ -Dicyno-1-hydroxycyclopentylethane- $\alpha$ : $\beta$ -dicarboxylic acid (BIRCH and THORPE), 1836.  
 Quinaldinic acid methonitrate (MILLS and HAMER), 2012

- $C_{11}H_{10}O_2Hg$ , 3:5-Diacetoxydimercuri-4-hydroxybenzaldehyde (HENRY and SHARP), 1058.  
 3:5-Diacetoxydimercurialicylaldehyde (HENRY and SHARP), 1056..  
 $C_{11}H_{10}O_2N_2$ , Dinitro-*m*-xylylpyruvic acid (DAVIES and HICKOX), 2646.  
 $C_{11}H_{11}O_2N$ , Methoxy-1-methylindole-2-carboxylic acid (KERMACK, PERKIN, and ROBINSON), 1881.  
 $C_{11}H_{13}NI$ , Methylisoquinoline methiodides (MILLS and SMITH), 2732.  
 $C_{11}H_{13}O_2N$ , Acetacet-*o*- and -*p*-toluidides (NAIK and AVASARE), 2594.  
 $C_{11}H_{13}O_2N_2$ , *N*-Methyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha\beta$ -trimethylglutaric acid (KON and THORPE), 1799.  
 $\omega$ -Imide of  $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid (KON and THORPE), 1800.  
 $C_{11}H_{13}O_2N$ , 2-Acetyl-amino-*p*-tolylloxyacetic acid (MINTON and STEPHEN), 1598.  
 $C_{11}H_{13}O_2N$ , 3-Carboxy-amino-4-methoxybenzoic acid (FROELICHER and COHEN), 1656.  
 Ethyl nitrotyloxyacetates (MINTON and STEPHEN), 1594.  
 $C_{11}H_{13}O_2N_2$ , Pyruvic acid *m*-methoxyphenylmethylhydrazone (KERMACK, PERKIN, and ROBINSON), 1881.  
 $C_{11}H_{13}O_2N_2$ ,  $\alpha\beta$ -Dicyano- $\gamma$ -hydroxy- $\gamma$ -ethylpentane- $\alpha\beta$ -dicarboxylic acid (BIRCH and THORPE), 1827.  
 $C_{11}H_{13}ON$ , Acetone-5-benzylsemicarbazone (WILSON, HOPFER, and CRAWFORD), 867.  
 Substance, from *cyclohexanespirocyclopentane*-3:4-dione semicarbazone and mineral acids (KON), 522.  
 $C_{11}H_{13}O_2N_2$ , *p*-Nitrobenzaldehydediethylhydrazone, and its salts (BRADY and McHUGH), 1651.  
 $C_{11}H_{13}O_2N$ , Ethyl  $\alpha$ -cyano- $\beta$ -methylglutaconate, and its action with ammonia and with water (HOPE), 2216.  
 $C_{11}H_{13}N_2S$ , Acetone-*S*-benzylthiosemicarbazone (WILSON and BURNS), 873.  
 $C_{11}H_{13}O_2N_2$ , Semicarbazone of  $\alpha$ -keto- $\alpha$ -campholenic acid (CHANDRASENA and INGOLD), 1555.  
 $C_{11}H_{13}O_2N$ , Ethyl  $\alpha$ -cyano- $\gamma$ -ethylglutaconate (INGOLD, PERREN, and THORPE), 1782.  
 $C_{11}H_{13}O_2N_2$ , *cyclo*Pentanespirocyclopentane-3:4-dione disemicarbazone (KON), 526.  
 $C_{11}H_{13}ON$ , *dl*-Piperitone semicarbazones (READ and SMITH), 1866.  
 $C_{11}H_{13}O_2N_2$ , Semicarbazone of *d*-1:1-dimethyl-2- $\gamma$ -ketobutylcyclopropane-3-carboxylic acid (SIMONSEN), 2295.  
 Semicarbazone of methyl 1:1-diethylcyclobutan-3-one-2-carboxylate (DICKENS, KON, and THORPE), 1504.  
 $C_{11}H_{13}O_2N_2$ , Disemicarbazone of 1:1-diethylcyclopentane-3:4-dione (DICKENS, KON, and THORPE), 1506.  
 $C_{11}H_{13}O_2N_2$ , Semicarbazido-*dl*-piperitone, and its hydrochloride (READ and SMITH), 1869.

II IV

- $C_{11}H_8O_2N_2Cl_2$ , Citraconyl-2:4-dichlorophenylhydrazides (CHATTAWAY and PARKES), 287.  
 $C_{11}H_8O_2N_2Br_2$ ,  $\alpha$ -Citraconyl-2:4-dibromophenylhydrazide (CHATTAWAY and PARKES), 287.  
 $C_{11}H_8O_2NSe$ , Cyano-3-selenium benzoylacetone (MORGAN, DREW, and BARKER), 2455.  
 $C_{11}H_8O_2N_2Cl$ , Citraconylchlorophenylhydrazides (CHATTAWAY and PARKES), 286.

- $C_{11}H_7O_2N_2Br$  Citraconylbromophenylhydrazides (CHATTAWAY and PARKES), 287.  
 $C_{11}H_7O_2N_2S_2$  Dinitrodithioaceto-*p*-toluidide (NAIK and AVASARE), 2595.  
 $C_{11}H_{11}O_2NCl$  Quinaldinic acid methochloride (MILLS and HAMER), 2012.  
 $C_{11}H_{11}O_2NS_2$  Dithioacetoaceto-toluidides (NAIK and AVASARE), 2594.  
 $C_{11}H_{11}O_2N_2Cl$  Citraconic acid *p*-chlorophenylhydrazide (CHATTAWAY and PARKES), 285.  
 $C_{11}H_{11}O_2N_2Br$  Citraconic acid *p*-bromophenylhydrazide (CHATTAWAY and PARKES), 286.  
 $C_{11}H_{11}NIS$  Phenylmethylthiazole methiodides (MILLS and SMITH), 2735, 2737.  
 $C_{11}H_{11}O_2N_2Cl$  *p*-Chlorophenylhydrazine citraconate (CHATTAWAY and PARKES), 285.  
 $C_{11}H_{11}NIS$  1:5-Dimethylbenzothiazole ethiodide (MILLS), 463.  
 $C_{11}H_{11}O_2NS_2$  Diethylsulphine-*p*-toluenesulphonylimine (MANN and POPE), 1053.

## II V

- $C_{11}H_{11}O_2NCl_2S_2$  *BB'*-Dichlorodiethylsulphine-*p*-toluenesulphonylimine (MANN and POPE), 1053.

**C<sub>12</sub> Group.**

- $C_{12}H_7N_3$  Carbazole-3-diazoimine (MORGAN and READ), 2712.  
 $C_{12}H_7N_3$  3-Triazocarbazole (MORGAN and READ), 2714.  
 $C_{12}H_{10}O_2$  Methoxyuaphthoic acids, preparation of (FROELICHER and COHEN), 1656.  
 $C_{12}H_{15}N_2$  Harmine (KERMACK, PERKIN, and ROBINSON), 1872.  
 $C_{12}H_{10}Pb$  Lead diphenyl, salts of, with organic acids (GODDARD, ASHLEY, and EVANS), 981.  
 $C_{12}H_{12}O_2$  Ethyl 2-hydrindene-1-carboxylate (PERKIN and TITLEY), 1566.  
 $\alpha$ -1-Ketotetrahydronaphthalene-3-acetic acid (STEVENSON and THORPE), 1721.  
 $C_{12}H_{12}O_4$  Acetoxybenzanthronecarboxylic acid (BRADSHAW and PERKIN), 914.  
 $C_{12}H_{12}O_{10}$   $\gamma$ : $\delta$ -Dihydroxy- $\Delta^2$ - $\gamma$ -octatriene- $\alpha$ : $\delta$ : $\delta$ : $\delta$ -tetracarboxylic acid (CHANDRASENA and INGOLD), 1319.  
 $C_{12}H_{12}N_2$  Benzidine, hydroferrocyanide of (CUMMING), 1296.  
 $C_{12}H_{14}O_2$  Methyl 1-methyl-1-ethylcyclopentane-3:4-dione-2:5-dicarboxylate (DICKENS, KON, and THORPE), 1503.  
 $C_{12}H_{14}O_2$  *cis*- and *trans*-2:4-Dicarboxycyclobutane-1:3-di- $\alpha$ -propionic acids (INGOLD, PERREN, and THORPE), 1737.  
 $C_{12}H_{14}N_2$  Dinitrile of 1-methyl-1-*n*-hexylcyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1828.  
 $C_{12}H_{14}O_2$  *cis*-1-Methyl-1-*n*-hexylcyclopropane-2:3-dicarboxylic anhydride (BIRCH and THORPE), 1829.  
 $C_{12}H_{16}O_2$  Ethyl *d*-1:1-dimethyl-2- $\gamma$ -ketobutylcyclopropane-3-carboxylate (SIMONSEN), 2297.  
 $C_{12}H_{16}O_4$   $\alpha$ -Ethylcyclohexane-1:1-diacetic acid (KON and THORPE), 1802.  
 $\gamma$ -Hydroxy- $\gamma$ -methylnonane- $\alpha$ : $\delta$ -dicarboxylic lactone (BIRCH and THORPE), 1830.  
 Methyl cyclohexane-1:1-diacetate (DICKENS, KON, and THORPE), 1505.  
*cis*- and *trans*-1-Methyl-1-*n*-hexylcyclopropane-2:3-dicarboxylic acids (BIRCH and THORPE), 1829.  
 $C_{12}H_{16}O_3$  Methyl trimethyltricarballoylate (HOPE and SHELTON), 2235.

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12 II-12 IV

- $C_{12}H_{21}O_{11}$  Sucrose, inversion of (MORAN and LEWIS), 1613; oxidation of, by nitric acid (CHATTAWAY and HARRIS), 2709.  
 $C_{12}H_{24}O_2$  Lauric acid, potassium salt, ultra-filtration of solutions of (McBAIN and JENKINS), 2325; sodium salt, equilibrium of sodium chloride, water, and (McBAIN and BURNETT), 1320.

12 III

- $C_{12}H_{10}N_2$  Dipicrylamine, cobaltamine salts of (MORGAN and KING), 1726.  
 $C_{12}H_8ON$  *N*-Nitrosocarbazole (MORGAN and READ), 2712.  
 $C_{12}H_8ON_2$  Carbazole-3-diazonium hydroxide, salts of (MORGAN and READ), 2711.  
 $C_{12}H_9O_2N$  4-Nitro-1-methoxy-2-naphthoic acid (FROELICHER and COHEN), 1657.  
 $C_{12}H_9N_2Cl$  3-Chloro-1-methyl-4-carboline (KERMACK, PERKIN, and ROBINSON), 1885.  
 $C_{12}H_{10}O_2S_2$  Di-*m*-hydroxyphenyl disulphide (WATSON and DUTT), 2415.  
 $C_{12}H_8O_2N_2$  Benzeneazohydroxyquinol (MUKERJI), 551.  
 $C_{12}H_{10}O_4N_2$  6-Carbamido-2-hydroxy-3-naphthoic acid (FROELICHER and COHEN), 1660.  
 $C_{12}H_9ON_2$  *p*-Nitrobenzenehydrazo-*o*-nitrophenol (MUKERJI), 2831.  
 $C_{12}H_8Cl_2I$  Thallium diphenyl chloride (GODDARD), 40.  
 $C_{12}H_8Br_2I$  Thallium diphenyl bromide (D. and A. E. GODDARD), 258.  
 $C_{12}H_8ON$   $\alpha\beta$ -Naphthadihydroisooxazine (CLEMO and PERKIN), 647.  
 $C_{12}H_9OCl$   $\alpha$ - and  $\beta$ -Naphthyl  $\beta$ -chloroethyl ethers (CLEMO and PERKIN), 646.  
 $C_{12}H_{17}O_2N$  Quinaldinic acid ethyl betaine (MILLS and HAMER), 2014.  
 $C_{12}H_{11}O_2N$  Aminomethoxynaphthoic acids (FROELICHER and COHEN), 1658.  
 $C_{12}H_{10}O_2N_2$  Citraconyltolylhydrazides (CHATTAWAY and PARKES), 288.  
 $C_{12}H_{11}N_2S$  4-Benzeneazo-1-naphthyl mercaptan (WATSON and DUTT), 1940.  
 $C_{12}H_{11}ON$  Ethoxyquinaldines, and their salts (BRAUNHOLTZ), 170.  
 $C_{12}H_{15}O_4Br$  8-Bromo- $\gamma\delta$ -dihydroxy- $\Delta^8$ -octadiene- $\alpha\beta\epsilon\theta$ -tetracarboxylic acid (CHANDRASENA and INGOLD), 1318.  
 $C_{12}H_7O_2N_2$  Citraconic acid *o*-tolylhydrazide (CHATTAWAY and PARKES), 287.  
 $C_{12}H_{16}O_4N_2$  Ethyl  $\alpha\beta$ -dicyano- $\beta$ -methylglutarate, preparation of (HOPE and SHELTON), 2226.  
 $C_{12}H_{16}O_4Br_2$  Ethyl dibromodiacetylsuccinate, preparation of (HIRST and MACBETH), 2175.  
 $C_{12}H_{17}ON_2$  Acetone- $\delta$ - $\alpha$ -phenylethylsemicarbazones (WILSON, HOPFER, and CRAWFORD), 869.  
 $C_{12}H_{15}O_4Se$  Selenium *C*-ethyl-*OC*-bisacetylacetone (MORGAN, DREW, and BARKER), 2451.  
 $C_{12}H_{17}ON_2$  2,8-Dicyano-1-methyl-1-*n*-hexylcyclopropane-2-carboxylamide (BIRCH and THORPE), 1827.  
 $C_{12}H_{20}O_2N_2$  *cyclo*Hexanespirocyclopentane-3,4-dione disemicarbazone (KON), 522.  
 $C_{12}H_{17}O_2N$  Amide of *trans*-1-methyl-1-*n*-hexylcyclopropane-2,3-dicarboxylic acid (BIRCH and THORPE), 1828.  
 $C_{12}H_{17}O_2N_2$  *trans*-1-Methyl-1-*n*-hexylcyclopropane-2,3-dicarboxylamide (BIRCH and THORPE), 1828.

12 IV

- $C_{12}H_9O_2N_2Mg$  Magnesium nitrophenoxides (GODDARD and WARD), 264.  
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- $C_{10}H_6O_2N_2Pb$ , Lead *m*- and *p*-nitrophenoxide (GODDARD and WARD), 264.  
 $C_{12}H_8Cl_2BrI$ , Di-*p*-chlorophenylbromobismuthine (CHALLENGER and RIDGWAY), 110.  
 $C_{12}H_8Cl_2IBI$ , Di-*p*-chlorophenyl iodobismuthine (CHALLENGER and RIDGWAY), 110.  
 $C_{12}H_8ONCl$ , 4'-Chloro-2-benzeneazophenol (CHATTAWAY and HILL), 2757.  
 $C_{12}H_8ONBr$ , 4'-Bromo-2-benzeneazophenol (CHATTAWAY and HILL), 2758.  
 $C_{12}H_8ONI$ , 4'-Iodo-2-benzeneazophenol (CHATTAWAY and HILL), 2758.  
 $C_{12}H_8ONS$ , Diphenyl-4:4'-bisazohydroxy-2-phenyl mercaptan (WATSON and DUTT), 2415.  
 $C_{12}H_8O_2NS$ , 3-Nitro-4-thiolbenzeneazo-4-hydroxy-2-phenyl mercaptan (WATSON and DUTT), 2417.  
 $C_{12}H_{10}ONCl$ , 1-Nitro- $\beta$ -naphthyl  $\beta$ -chloroethyl ether (CLEMO and PERKIN), 646.  
 $C_{12}H_{10}ONCl$ , 1-Amino- $\beta$ -naphthyl  $\beta$ -chloroethyl ether (CLEMO and PERKIN), 647.  
 $C_{12}H_{10}ONBr$ , 4-Bromo-5:8-dihydroaceto- $\alpha$ -naphthalide (ROWE and DAVIES), 1006.  
 $C_{12}H_{10}ONBr$ , 4:6:7-Tribromotetrahydroaceto- $\alpha$ -naphthalide (ROWE and DAVIES), 1006.  
 $C_{12}H_{12}ONCl$ , Quinaldinic acid ethochloride (MILLS and HAWES), 2013.  
 $C_{12}H_{12}O_2NI$ , Methyl quinaldinate methiodide (MILLS and HAWES), 2011.  
 $C_{12}H_{12}ONBr$ , 6:7-Dibromotetrahydroaceto- $\alpha$ -naphthalide (ROWE and DAVIES), 1005.  
 $C_{12}H_{13}O_2NS$ , *N*- $\alpha$ -Naphthyl- $\beta$ -aminoethyl hydrogen sulphate (SAUNDERS), 2675.

## 12 V

- $C_{12}H_5O_2N_2Se_2Cu$ , Copper cyano-3-selenium acetylacetone (MORGAN, DEWE, and BARKER), 2448.

 **$C_{12}$  Group.**

- $C_{12}H_8O$ , 1:3-Dihydroxyxanthone ( $+H_2O$ ) (NISHIKAWA and ROBINSON), 841.  
 $C_{12}H_8N_4$ , Carbazole-3-diazoeyanide (MORGAN and READ), 2714.  
 $C_{12}H_{10}O_2$ , Tetrahydroxybenzophenones (NISHIKAWA and ROBINSON), 842.  
 Substance, from oxidation of the lactone of 3-hydroxy-2-*o*-carboxybenzyl-2-methylcyclopropane-1-carboxylic acid (KON, STEVENSON, and THORPE), 663.  
 $C_{12}H_{10}Cl$ , Benzophenone chloride, action of sodium methoxide and its homologues on (MACKENZIE), 1695.  
 $C_{12}H_{12}O$ , *cis*-1-Benzyl-1-methylcyclopropane-2:3-dicarboxylic anhydride (BIRCH and THORPE), 1833.  
 $C_{12}H_{12}O_4$ , Lactone of 3-hydroxy-2-*o*-carboxybenzyl-2-methylcyclopropane-1-carboxylic acid, and its silver salt (KON, STEVENSON, and THORPE), 662.  
 Lactone of *ac*-1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic acid, and its silver salt (KON, STEVENSON, and THORPE), 660.  
 $C_{12}H_{12}O_2$ , *p*-Methoxycinnamylidenemalononic acid (HIGGINOTHAM and LAYWORTH), 2828.  
 $C_{12}H_{12}O_4$ , Methylenebis-2:3:5:6-tetrahydroxybenzene (MUKERJI), 549.  
 $C_{12}H_{12}N_4$ , Dinitrile of *trans*-1-benzyl-1-methylcyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1831.  
 $C_{12}H_{14}O_2$ , Ethyl 1-methyl-2-hydrindone-1-carboxylate (PERKIN and TITLER), 1669.

- $C_{15}H_{14}O_4$  *cis*- and *trans*-1-Benzyl-1-methylcyclopropane-2:3-dicarboxylic acids (BIRCH and THORPE), 1832.  
 $\gamma$ -Hydroxy- $\gamma$ -benzylbutane- $\alpha\beta$ -dicarboxylic lactone (BIRCH and THORPE), 1833.  
 $C_{15}H_{14}O_4$   $\alpha$ -o-Carboxybenzyl- $\alpha$ -methylsuccinic acid (KON, STEVENSON, and THORPE), 662.  
 $C_{15}H_{14}N_2$  Quinoxaline derivative of 1:1-dimethylcyclopentane-3:4-dione (KON), 624.  
 $C_{15}H_{14}O_4$  Ethyl homophthalate, preparation of (DAVIES and PERKIN), 2208.  
 $C_{15}H_{14}O_4$  Methyl cyclopentanespirocylopentane-3:4-dione-2:5-dicarboxylate (DICKENS, KON, and THORPE), 1562.  
 $C_{15}H_{14}O_4$  Ethyl 1:4-dimethyl-1-cyclohexane-3:5-dione-2-carboxylate (BECKER and THORPE), 1304.  
 $C_{15}H_{14}O_4$   $\gamma\delta$ -Diacetoxydihydro- $\alpha$ -campholytic acid (CHANDRASENA, INGOLD, and THORPE), 1549.  
 Ethyl isobutylene tricarboxylate (INGOLD and NICKOLLS), 1645.  
 $C_{15}H_{14}O_5$  Ethyl 3:3-diethylcyclopropanol-1:2-dicarboxylate (DESHAPANDE and THORPE), 1441.

13 III

- $C_{15}H_9O_2N$  Nitro- $\beta$ -naphthacoumarin (MORGAN and BREVES), 7.  
 $C_{15}H_9O_2N_2$  2:4-Dinitrobenzaldoxime-*N*-nitrophenyl ethers (BARROW, GRIFFITHS, and BLOOM), 1716.  
 $C_{15}H_9O_2N_2$  *m*- and *p*-Nitrobenzylidenenitroanilines (INGOLD and PIGGOTT), 2799.  
 $C_{15}H_9O_2N_2$  Dinitrobenzaldoxime-*N*-phenyl ethers (BARROW, GRIFFITHS, and BLOOM), 1714.  
 2:4-Dinitrobenzanilide (BARROW, GRIFFITHS, and BLOOM), 1714.  
*m*-Nitrobenzenesazosalicylic acid, chromic and cobaltamine salts of (MORGAN and SMITH), 2870.  
 $C_{15}H_9O_2N_2$  Benzylidene-*o*-nitroaniline (INGOLD and PIGGOTT), 2804.  
 $C_{15}H_9O_2N_2$  *p*-Hydroxybenzylidene-*m*-nitroaniline (INGOLD and PIGGOTT), 2799.  
 $C_{15}H_{10}NBI$  Diphenylcyanobismuthine (CHALLENGER and WILKINSON), 98.  
 $C_{15}H_{11}O_4N$  2:4:6:2'-Tetrahydroxydiphenyl ketimine, and its hydrochloride (NISHIKAWA and ROBINSON), 840.  
 $C_{15}H_7O_2N$  2-Carboxyindole-1:3-diacetic acid (KERMACK, PERKIN, and ROBINSON), 1893.  
 $C_{15}H_{10}ON_2$  5-Keto-4:7-dimethyl-4:5-dihydroindolediazine(1:4) (KERMACK, PERKIN, and ROBINSON), 1888.  
 2-*o*-Tolueneazophenol (CHATTAWAY and HILL), 2758.  
 $C_{15}H_{11}O_2N_2$  11-Methoxy-3-keto-4-methyl-3:4-dihydro-4-carboline (KERMACK, PERKIN, and ROBINSON), 1889.  
 11-Methoxy-5-keto-4-methyl-4:5-dihydroindolediazine(1:4) (KERMACK, PERKIN, and ROBINSON), 1890.  
 $C_{15}H_{13}O_2N_2$  Carbamido-1-methoxynaphthoic acids (FROELICHER and COHEN), 1858.  
 $C_{15}H_{13}O_2N$  Imide of 1-benzyl-1-methylcyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1832.  
 $C_{15}H_{13}O_2N$  Oxime of  $\alpha$ -1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic lactone (KON, STEVENSON, and THORPE), 662.  
 $C_{15}H_{13}O_2N_2$  Nitroacetanilide- $\omega$ -pyridinium hydroxides, salts of (BARNETT and COOK), 794.  
 $C_{15}H_{11}ON_2$  Harmaline (KERMACK, PERKIN, and ROBINSON), 1872.

- $C_{11}H_{14}O_2N_2$  Acetanilide- $\omega$ -pyridinium hydroxide, salts of (BARNETT and COOK), 794.
- $C_{11}H_{14}O_3N_2$  Substance, from  $\alpha\alpha$ -dihydroxy- $\beta\beta$ -dimethylglutaric acid and *o*-phenylenediamine (KON, STEVENSON, and THORPE), 665.
- $C_{11}H_{14}O_4N_2$  2:3:5-Triketo-6- $\alpha$ -methoxybenzyl-1(or 4)-methylpiperazine (FORSTER and SAVILLE), 324.
- $C_{12}H_{14}O_4N_2$   $\alpha\beta$ -Dicyano-1-hydroxy-3- and -4-methylcyclohexylethane- $\alpha\beta$ -dicarboxylic acids (BIRCH and THORPE), 1836.
- $C_{11}H_{10}O_2N_2$  Semicarbazone of  $\alpha$ -1-ketotetrahydronaphthalene-3-acetic acid (STEVENSON and THORPE), 1721.
- $C_{12}H_{12}N_4S_2$  2:2':4:4'-Tetra-amino-5:5'-dithioldiphenylmethane (WATSON and DUTI), 1943.
- $C_{12}H_{14}ON_2$  *N*-Methyltetrahydronorharmine (KERMACK, PERKIN, and ROBINSON), 1891.
- $C_{12}H_{14}O_2N_2$  Indole-2-carboxydimethylacetamidamide (KERMACK, PERKIN, and ROBINSON), 1892.
- $C_{12}H_{17}O_2N_2$  *N*-Ethyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid (KON and THORPE), 1800.
- $C_{12}H_{17}O_4N$  Salicylidene glucosamine (IRVINE and EARL), 2378.
- $C_{12}H_{17}O_4N_2$  2:3-Dicyano-1-methyl-1-*n*-hexylcyclopropane-2-carboxylic acid, and its silver salt (BIRCH and THORPE), 1827.
- $C_{12}H_{17}O_4N_2$  Ethyl dicyanomethylbutanedicarboxylates (HOPE and SHELTON), 2229, 2232.
- $C_{12}H_{17}ON$   $\beta$ -Benzyloxytriethylamine (CLEMO and PERKIN), 649.
- $C_{12}H_{17}O_2N$  Ethyl piperidinomethylenemalonate (INGOLD, PERREN, and THORPE), 1785.
- $C_{12}H_{17}O_4N$  3:5:6-Triacetyl-1-methyl glucosamine (IRVINE and EARL), 2381.
- $C_{12}H_{17}O_4Br_2$  Ethyl  $\alpha\alpha'$ -dibromo- $\beta\beta$ -diethylglutarate (DESHAPANDE and THORPE), 1436.
- $C_{12}H_{17}O_4N_2$  Semicarbazone of ethyl *d*-1:1-dimethyl-2- $\gamma$ -ketobutylcyclopropane-3-carboxylate (SIMONSEN), 2297.
- $C_{12}H_{17}O_4Sn$  Penta-acetyl derivative of methylstannonic acid (LAMBOURNE), 2537.

## 13 IV

- $C_{12}H_{11}O_2N_2Br$  *m*-Nitrobenzylidene-*p*-bromoaniline (INGOLD and PIGGOTT), 2800.
- $C_{12}H_{11}ONBr$  *p*-Hydroxybenzylidene-*p*-bromoaniline (INGOLD and PIGGOTT), 2798.
- $C_{12}H_{11}NSBI$  Diphenylthiocyanobismuthine (CHALLENGER and WILKINSON), 98.
- $C_{12}H_{11}O_2NCl$  Phenyl acetate- $\omega$ -pyridinium chloride (+3H<sub>2</sub>O) (BARNETT and COOK), 797.
- $C_{12}H_{11}O_2NCl$  Ethyl 5-chloro-2:4-dinitro-6-methylphenylacetoacetate (DAVIES and HICKOX), 2647.
- $C_{12}H_{11}O_4ClSn$  Chloroacetyl derivative of methylstannonic acid (LAMBOURNE), 2538.

## 13 VI

- $C_{12}H_{11}O_2NCl_3SAs$   $\beta\beta'\beta''$ -Trichlorotrivinylarsine-*p*-toluenesulphonylimine (MANN and POVE), 1758.

**C<sub>14</sub> Group.**

- $C_{14}H_{10}$  Phenanthrene, solubility of, in organic solvents (HENSTOCK), 2124.

14 II

- $C_{14}H_6O$ , 1:2:4-Trioxo-5:8-dihydroxyanthraquinone, aminocobaltic salt (MORGAN and SMITH), 168.  
 $C_{14}H_4O_4$ , 1:2-Dioxanthraquinone, 2-pentammino-1:2-dicobaltic salt (MORGAN and SMITH), 166.  
 $C_{14}H_2O_4$ , 1:2-Dioxhydroxyanthraquinones, cobalt and aminocobalt salts (MORGAN and SMITH), 166.  
 $C_{14}H_2O_4$ , 1:2-Dioxo-5:8-dihydroxyanthraquinone, 2-pentammino-1:2-dicobaltic salt (MORGAN and SMITH), 167.  
 $C_{14}H_2O_2$ , 2-Hydroxyanthraquinone, reduction of (PERKIN and WHATTAM), 289.  
 $C_{14}H_2Cl_2$ , Dichloroanthracene, preparation of (BARNETT, COOK, and GRAINGER), 2088.  
 $C_{14}H_2Br_2$ , Dibromoanthracene, preparation of (BARNETT, COOK, and GRAINGER), 2085.  
 $C_{14}H_2O_2$ , Diacetylacetone, preparation of, and its salts (COLLIE and HILLY), 1984.  
 $C_{14}H_{10}O$ , Substance, from ethyl 5-aldehydosalicylate and acetylacetone (WAYNE and COHEN), 1027.  
 $C_{14}H_{10}O_4$ ,  $\gamma$ -Hydroxy- $\gamma$ -benzylbutane- $\alpha\beta$ -tricarboxylic lactone (BIRCH and THORPE), 1833.  
 $C_{14}H_{11}N$ ,  $\alpha$ -Tolidine, hydroferrocyanide of (CUMMING), 1298.  
 $C_{14}H_{11}O_4$ , Diethyl  $\alpha$ -phenylenediacetate (PERKIN and TILLEY), 1565.  
 $C_{14}H_{20}O_4$ , Tetra-acetylacritol (PERKIN and UYEDA), 71.  
 $C_{14}H_{20}O_4$ , Menthyl hydrogen succinate (SHIMOMURA and COHEN), 2056.  
 $C_{14}H_{20}O_4$ , Ethyl  $\beta$ -methylmethanetriacetate (INGOLD), 1149.

14 III

- $C_{14}H_6O_4N$ , 1:2-Dioxo-3-nitroanthraquinone, 2-pentammino-1:2-dicobaltic salt (MORGAN and SMITH), 166.  
 $C_{14}H_4O_4S$ , 1:2-Dioxanthraquinone-3-sulphonic acid, 2:3-dipentammino-1:2:3-tricobaltic salt (MORGAN and SMITH), 167.  
 $C_{14}H_4O_4N_4$ , 4:6:4':6'-Tetranitrodiphenic acid, resolution of, and its salts (CHRISTIE and KENNER), 614.  
 $C_{14}H_6O_4N$ , 1:2-Dioxo-3-aminoanthraquinone, 2-tetrammino-1:2-dicobaltic salt (MORGAN and SMITH), 168.  
 $C_{14}H_2O_4N_2$ , Dinitroanthracene, preparation of (BARNETT, COOK, and GRAINGER), 2085.  
 $C_{14}H_2O_4N_2$ , 2:4-Dinitrobenzil (BISHOP and BRADY), 2368.  
 $C_{14}H_2O_4N_2$ ,  $\gamma$ :6:6'-Dinitrodiphenic acid, resolution of, and its salts (CHRISTIE and KENNER), 614.  
 $C_{14}H_2O_4N_2$ , Tetranitrostilbenes (BISHOP and BRADY), 2367.  
 $C_{14}H_2O_4N_2$ , 2:4-Dinitrobenzilmonoximes (BISHOP and BRADY), 2368.  
 $C_{14}H_{10}O_4S_2$ ,  $p$ -Disulphidobenzoic acid (SMILES and HARRISON), 2022.  
 $C_{14}H_{11}O_4N_2$ , Benzeneazo-4-oxybenzenedicarboxylic acid, cobaltamine salts of (MORGAN and SMITH), 2872.  
 $C_{14}H_{11}O_4N_2$ , Nitrobenzylidenenitrobenzylamines (INGOLD and PIGGOTT), 2386, 2891.  
 $C_{14}H_{11}O_4N_2$ , 2:4-Dinitrobenzaloxime- $N$ -tolylethers (BARROW, GRAYFITHS, and BLOOM), 1715.  
 $C_{14}H_{11}O_4N_2$ , Benzylidenenitrobenzylamines, and Nitrobenzylidenenitrobenzylamines (INGOLD and PIGGOTT), 2385.  
 $C_{14}H_{11}O_4N_2$ , Nitrophenoxycetanilides (MINTON and STEPHEN), 1594.



- $C_{14}H_{13}O_4N_4$  2:4-Dinitrobenzaldoxime-*N-p*-methylaminophenyl ether (BARROW, GRIFFITHS, and BLOOM), 1716.
- $C_{14}H_{13}ON_2$  2:3-Dicyano-1-benzyl-1-methylcyclopropane-2-carboxylamide (BIRCH and THORPE), 1830.
- N*-Ethylcarbazole-3-diazonium hydroxide, salts of (MORGAN and REARD), 2715.
- $C_{14}H_{14}O_4S_2$  Benzyl disulphoxide, decomposition of (SMYTHE), 1406.
- $C_{14}H_{14}N_4S$  3-Amino-7-dimethylamino-4-thiophenazine (WATSON and DUFF), 1941.
- $C_{14}H_{14}ClTI$  Thallium di-*o*- and -*p*-tolyl chlorides (D. and A. E. GODDARD), 258.
- $C_{14}H_{14}BrTI$  Thallium di-*p*-tolyl bromide (D. and A. E. GODDARD), 258.
- $C_{14}H_{14}ClBI$  Dip-tolylchlorobismuthine (CHALLENGER and RIDGWAY), 113.
- $C_{14}H_{15}ON$   $\beta$ -Phenoxyethylaniline (CLEMO and PERKIN), 645.
- $C_{14}H_{15}O_4N_2$  Semicarbazone of  $\alpha$ -1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic lactone (KON, STEVENSON, and THORPE), 682.
- $C_{14}H_{16}O_4N_4$  Aceto-*o*- and -*p*-toluidide- $\alpha$ -pyridinium hydroxides, salts of (BARNETT and COOK), 794.
- $\alpha$ -Dianisidine, hydroferrocyanide of (CUMMING), 1296.
- $C_{14}H_{16}O_4N_2$  Substance, from  $\alpha$ -keto- $\beta\beta\gamma$ -trimethylsuccinic acid and *o*-phenylenediamine (KON, STEVENSON, and THORPE), 664.
- $C_{14}H_{16}O_4N_2$  2:3:5-Triketo-6- $\alpha$ -methoxybenzyl-1:4-dimethylpiperazine (FORSTER and SAVILLE), 824.
- Diamide of 1-benzyl-1-methylcyclopropane-2:2:3-tricarboxylic acid (BIRCH and THORPE), 1831.
- $C_{14}H_{17}ON$   $\beta$ -Naphthyl- $\beta$ -dimethylaminoethyl ether, hydrochloride of (CLEMO and PERKIN), 646.
- $C_{14}H_{17}O_4N_2$   $\omega$ -Imide of  $\alpha\alpha'$ -dicyano- $\alpha\alpha'$ -dimethylcyclohexane-1:1-diacetic acid (KON and THORPE), 1802.
- $\omega$ -Imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -ethylcyclohexane-1:1-diacetic acid (KON and THORPE), 1802.
- N*-Methyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -methylcyclohexane-1:1-diacetic acid (KON and THORPE), 1801.
- $C_{14}H_{17}O_4N_2$  Ethyl 1-methyl-2-hydrindone-1-carboxylate semicarbazone (PERKIN and TITLEY), 1570.
- $C_{14}H_{17}O_4N$  Indican, constitution of (MACBETH and PRYDE), 1650.
- 2-Salicylidene-1-methyl glucosamine (IRVINE and EARL), 2379.
- $C_{14}H_{17}O_4N_2$  Indole-2-carboxydimethylacetyl methylamide (KERMACK, PERKIN, and ROBINSON), 1886.
- 3-Keto-4-methyl-3:4-dihydro-4- $\alpha$ -carboline (KERMACK, PERKIN, and ROBINSON), 1887.
- $C_{14}H_{19}O_4N_2$  Ethyl  $\beta\gamma$ -dicyano- $\gamma$ -methylpentane- $\beta\beta$ -dicarboxylate (HOPE and SHELTON), 2231.
- $C_{14}H_{19}O_4N_2$   $\alpha\beta$ -Dicyano- $\gamma$ -hydroxy- $\gamma$ -methylnonane- $\alpha\beta$ -dicarboxylic acid (BIRCH and THORPE), 1830.
- Substance, from  $\alpha$ -keto- $\beta\beta\gamma$ -trimethylsuccinic acid and *p*-phenylenediamine (KON, STEVENSON, and THORPE), 664.
- $C_{14}H_{19}O_4N_2$   $\omega$ -Imide of  $\alpha\alpha'$ -dicarbonyl- $\alpha\alpha'$ -dimethylcyclohexane-1:1-diacetic acid (KON and THORPE), 1803.
- $C_{14}H_{20}O_4Se$  Selenium bis-*C*-ethylacetylacetone (MORGAN, DREW, and BARKER), 2461.
- $C_{14}H_{20}O_4Se_2$  Diselenium bis-*C*-ethylacetylacetone (MORGAN, DREW, and BARKER), 2464.
- $C_{14}H_{20}O_4N_2$  Semicarbazone of the oxalyl derivative of ethyl glutarate (DICKENS, KON, and THORPE), 1501.

$C_{11}H_{10}OS_{11}$  Substance, from potassium dithioethylene glycol and chloropicrin (RAY and DAs), 326.

14 IV

$C_{11}H_8O_4N_2Cl$  Substance, from *o*-2:4-dinitrobenzoxime and phosphorus pentachloride (BISHOP and BRADY), 2369.

$C_{11}H_{10}O_4N_2Cl$  Nitrophenylhydrazones of chlorocoumaran-2-ones (MINTON and STEPHEN), 1602.

$C_{11}H_{10}O_4N_2Cl_2$  2:2'-Dichloro-8:8'-dinitro-4:4'-ditolyl (BURTON and KENNEDY), 496.

$C_{11}H_{12}ON_2Cl$  *p*-Chloroacetylaminoozobenzene (BARNETT and COOK), 795.

$C_{11}H_{13}ON_2Cl$  Chlorophenoxyacetanilides (MINTON and STEPHEN), 1601.

$C_{11}H_{11}O_4N_2S$  *g*-Dimethylamino-2-thiol-3-phenoxazone (WATSON and DUFF), 1942.

$C_{11}H_{13}ON_2Cl$  *o*-Acetoxybenzoic acid  $\pi$ -pyridinium chloride (BARNETT and COOK), 797.

$C_{11}H_{11}O_4N_2Pb$  Lead nitrotolylloxides (GODDARD and WARD), 265.

$C_{11}H_{11}O_4N_2Pb$  Lead dinitro-*o*-tolylloxide (GODDARD and WARD), 265.

$C_{11}H_{11}O_4N_2S$  Methyl-orange, use of, as an indicator (HICKMAN and LINSTEAD), 2502.

$C_{11}H_{11}ON_2I$  Ethoxyquinaldine ethiodides (BRAUNHOLTZ), 170.

$C_{11}H_{11}N_2ClS$  Phenylhydrazinoethanesulphonylphenylhydrazide hydrochloride (CLUTTERBUCK and COHEN), 127.

$C_{15}$  Group.

$C_{15}H_{11}N$  2:3-Indeno(2:1)-indole (ARMIT and ROBINSON), 838.

$C_{15}H_{11}O_2$  2-Hydroxystyryl furfurylideneethyl ketone (BUCK and HEILBRON), 1100.

$C_{15}H_{11}O_4$  Acetyl derivative of *ac*-1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic lactone (KON, STEVENSON, and THORPE), 661.

$C_{15}H_{11}O_4$  Catechin, constitution of (NIERENSTEIN), 604.

$C_{15}H_{11}N_4$  Quinoxaline derivative of cyclopentanespirocyclopentane-3:4-dione (KON), 526.

$C_{15}H_{21}O_4$  Castelin (+ 3H<sub>2</sub>O) (BOSMAN), 970.

Ethyl hydrogen  $\Delta^6$ -butene- $\alpha\beta$ -dicarboxylate- $\beta$ -malonate (FARMER), 2018.

$C_{15}H_{21}O_4$  Menthyl acetylpyruvate (SHIMOMURA and COHEN), 2053.

15 III

$C_{11}H_8O_4Cl$  Chloro-1-benzylidenecoumaran-2-ones (MINTON and STEPHEN), 1602.

$C_{11}H_8O_4Cl$  Chloroflavonols (MINTON and STEPHEN), 1602.

$C_{11}H_{10}O_4N_2$  Phthalylphenylcarbamide (ELLIOTT), 206.

$C_{11}H_{10}N_2S_2$  Dibenzothiazolylmethane (MILLS), 464.

$C_{11}H_{11}O_4N$  Benzoylmandelonitrile, action of alcoholic sodium ethoxide on (GREENE and ROBINSON), 2182.

$C_{11}H_{11}O_4Cl$  Chlorodibenzoylmethane (MORGAN, DREW, and BARKER), 2463.

$C_{11}H_{11}O_4N_2$  Cinnamantaldoxime-2:4-dinitrophenyl ether (BRADY and THOMAS), 2106.

$C_{11}H_{11}O_4N_2$  2:4-Dinitrobenzilmonosemicarbazone (BISHOP and BRADY), 2370.

$C_{11}H_{13}O_4N_2$  Nitrophenylhydrazone of methyl aldehydosalicylate (WAYNE and COHEN), 1027.

$C_{11}H_{11}O_4N_2$  Phenylhydrazone of methyl 5-aldehydosalicylate (WAYNE and COHEN), 1026.

- $C_{14}H_{14}O_2N_2$  Nitrotololyoxyacetanilides (MINTON and STEPHEN), 1505.  
 $C_{14}H_{14}O_2N_2$   $\alpha\beta$ -Dicyano- $\gamma$ -hydroxy- $\gamma$ -benzylbutane- $\alpha\beta$ -dicarboxylic acid (BIRCH and THORPE), 1833.  
 $C_{14}H_{13}O_2N_2$  Dinitrobenzaldoxime-*N*-*p*-dimethylaminophenyl ethers (BARROW, GRIFFITHS, and BLOOM), 1715.  
 $C_{14}H_{13}O_2N_2$  2:4-Dinitrobenzaldoxime-*N*-*p*-ethylaminophenyl ether (BARROW, GRIFFITHS, and BLOOM), 1716.  
 $C_{14}H_{13}ON$  Benzylidene derivative of  $\delta$ -benzylsemicarbazide (WILSON, HOPPER, and CRAWFORD), 868.  
 $C_{14}H_{13}O_2N_2$  Aminomalonanilide (RENDALL and WHITELEY), 2110.  
 $C_{14}H_{13}O_2N$  Carbethoxyaminomethoxynaphthoic acids (FROELICHER and COHEN), 1658.  
 $C_{14}H_{13}N_2S$  Benzaldehyde-*S*-benzylthiosemicarbazone (WILSON and BURNS), 874.  
 $C_{14}H_{13}ON$  *r*- and *l*-Phenyl-*p*-tolylacetamides (McKENZIE and SMITH), 1357.  
 $C_{14}H_{13}N_2Cl_2$  Dibenzylcyanamide dihydrochloride (SHORT and SMITH), 1806.  
 $C_{14}H_{13}O_2N$  Anil of *cis*-3:3-diethylcyclopropane-1:2-dicarboxylic acid (DESHAPANDE and THORPE), 1438.  
 $C_{14}H_{13}O_2N$  Ethyl  $\alpha$ -cyano-*o*-carbethoxy- $\beta$ -phenylpropionate (DAVIES and PERKIN), 2210.  
 $C_{14}H_{13}O_2N$  *cyclo*Hexanespirocyclobutan-3-one *p*-nitrophenylhydrazone (KON), 521.  
 $C_{14}H_{13}O_2N$  Anilic acid from *cis*-3:3-diethylcyclopropane-1:2-dicarboxylic acid (DESHAPANDE and THORPE), 1438.  
 $C_{14}H_{13}O_2N$  Phenylhydrazone of ethyl 3-methylcyclobutan-1-one-3-acetate (INGOLD), 1152.  
 $C_{14}H_{13}O_2N$  Ethyl *o*-carbethoxybenzylmalonamate (DAVIES and PERKIN), 2210.  
 $C_{14}H_{13}ON$  Substance, from cyclohexanone and ethyl  $\alpha$ -cyanopropionate (KON and THORPE), 1802.  
 $C_{14}H_{13}O_2N$  6-Methoxyindole-2-carboxydimethylacetalylmethylamide (KERMACK, PERKIN, and ROBINSON), 1898.  
 $C_{14}H_{13}N_2S_2$   $\alpha\gamma$ -Propanedisulphonyldiphenylhydrazide (CLUTTERBUCK and COHEN), 127.  
 $C_{14}H_{13}O_2N$  Semianilide of  $\alpha$ -ethyl- $\beta\beta$ -dimethylglutaric acid (KON and THORPE), 1800.  
 $C_{14}H_{13}O_2N$  Ethyl  $\Delta$ -butene- $\alpha\beta$ -dicarboxylate- $\beta$ -cyanoacetate (FARMEN), 2017.  
 $C_{14}H_{13}O_2N$  3-Methylindole-2-carboxydimethylacetalylmethylamide (KERMACK, PERKIN, and ROBINSON), 1898.  
 $C_{14}O_2NFe_4$  Iron nitrosocarbonyl (MOND and WALLIS), 35.

## 15 IV

- $C_{15}H_9O_2ClBr$  Chloro-1-benzylidenecoumaran-2-one dibromides (MINTON and STEPHEN), 1802.  
 $C_{15}H_9O_2Cl_3Te$  Tellurium dibenzoylmethane trichloride (MORGAN and DREW), 939.  
 $C_{15}H_9O_2N_2Br$  Phenylhydrazone of methyl 5-bromoaldehydosalicylate (WAYNE and COHEN), 1024.  
 $C_{15}H_{11}O_2SSe$   $\alpha$ -Naphthylthioselenium acetylacetone (MORGAN, DREW, and BARKER), 2453.  
 $C_{15}H_{11}O_2N_2S$  Dimethylharminesulphonic acid (15H<sub>2</sub>O) (KERMACK, PERKIN, and ROBINSON), 1896.  
 $C_{15}H_{11}O_2N_2S_2$   $\alpha$ -Di-*p*-tolylcarbamide-2:2'-disulphonic acid, potassium salt (SCOTT and COHEN), 2041.

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15 IV—16 III

$C_{15}H_{17}O_4NS$  *N*-Phenyl-*N*-benzyl- $\beta$ -aminoethyl sulphate, sodium salt (SAUNDERS), 2674.

$C_{15}H_{24}ONI$   $\beta$ -Benzyl-oxytetraethylammonium iodide (CLEMO and PERKIN), 849.

15 V

$C_{15}H_{15}O_2N_2ClBr_2$  Chlorobromomalono-*p*-bromoanilide (WEST), 2201.

$C_{15}H_{15}O_2N_2Cl_2Br_2$  Dichloromalono-*p*-bromoanilide (WEST), 2201.

$C_{15}H_{15}O_2N_2ClBr_2$  Chloromalono-*p*-bromoanilide (WEST), 2201.

$C_{15}H_{15}O_2N_2BrS$  Benzoyl-*p*-bromophenylbiuret-*o*-sulphonic acid, potassium salt (+2 $\frac{1}{2}$ H<sub>2</sub>O) (SCOTT and COHEN), 2047.

$C_{15}H_{20}O_2N_2ClS_2$  Substance, from pinacolylthiocarbamide and chloropierin (RÄY and DAS), 326.

C<sub>16</sub> Group.

$C_{16}H_{12}O_2$  isoHæmatin (CRABTREE and ROBINSON), 1040.

2-Methoxyanthraquinone-1-carboxylic acid (BRADSHAW and PERKIN), 917.

$C_{16}H_{14}O_2$  isoBrazilein, synthesis of (CRABTREE and ROBINSON), 1033.

Benzoyl derivative of methyl-5-aldehydosalicylate (WAYNE and COHEN), 1023.

$C_{16}H_{14}N$  1-Methyl-2:3-indenoindoles (ARMIT and ROBINSON), 833.

$C_{16}H_{14}O_2$  Benzoylbenzoin, mechanism of the formation of (GREENE and ROBINSON), 2182.

$C_{16}H_{18}O_4$  *s*-Diphenylsuccinic acid, preparation of (LAPWORTH and McRAE), 1709.

$C_{16}H_{18}O_2$   $\beta$ -Gambier-catechincarboxylic acids, and their salts (NIZRENSTEIN), 26.

$C_{16}H_{18}S$  Dietylryl sulphide (POPE and SMITH), 1168.

$C_{16}H_{18}O$  Phenyl-*p*-methoxyphenyl- $\Delta^2$ -propenes (INGOLD and FERGOTT), 2336.

$C_{16}H_{18}N_2$  Quinoxaline derivative of cyclohexanespirocyclopentane-3:4-dione (KON), 523.

$C_{16}H_{18}N_2$  *d*-Carvotanacetonephenylhydrazone (SIMONSEN and RAY), 390.

$C_{16}H_{20}O_8$  Ethylisobutylene- $\alpha$ - $\gamma$ - $\gamma'$ -tetracarboxylate (INGOLD and NICKOLLS), 1643.

$C_{16}H_{20}O_2$  Substance, from hydrolysis of capsularin (SAHA and CHOUHURY), 1045.

$C_{16}H_{30}O_4$  Thapsic acid, electro-synthesis of (CARMICHAEL), 2545.

$C_{16}H_{30}O_2$  Palmitic acid, sodium salt, hydrolysis of solutions of (McBAIN, TAYLOR, and LAINO), 621.

16 III

$C_{16}H_{16}O_4N_2$  6:6'-Dinitropiperil (GREENE and ROBINSON), 2193.

$C_{16}H_{16}O_4N_2$  *p*-Nitrobenzenediazo-4-nitro-*a*-naphthol (MUKERJI), 2880.

$C_{16}H_{16}O_4N_2$  6:6'-Dinitropiperoin (GREENE and ROBINSON), 2192.

$C_{16}H_{16}O_4N_2$  8'-Nitropiperoin (GREENE and ROBINSON), 2191.

$C_{16}H_{16}O_4N_2$  *p*-Nitrobenzenehydrazo-4-nitro-*a*-naphthol (MUKERJI), 2881.

$C_{16}H_{16}N_2S_2$  2-Methylbenzothiazolonylbenzothiazoly(methane (MILLS), 465.

$C_{16}H_{16}O_2N$  *s*-Diphenylsuccinimide (LAPWORTH and McRAE), 1712.

$C_{16}H_{16}O_2N_2$  Carbanilinonitrocinnamaldioximes (BRADY and THOMAS), 2108.

$C_{16}H_{16}N_2Cl$  Quindoline methochloride (ARMIT and ROBINSON), 837.

$C_{16}H_{16}O_2N_2$  Carbanilinocinnamaldioximes (BRADY and THOMAS), 2104.

$C_{16}H_{16}O_2N_2$  Acetyl-2:4-dinitrohydrobenzoin (BISHOP and BRADY), 2367.

- $C_{16}H_{11}ON$  Cinnamaldioxime benzyl ethers (BRADY and THOMAS), 2106.  
 $C_{16}H_{11}O_2N$  *iso*Nitrosomalonanilide methyl ethers (RENDALL and WHITELEY), 2115, 2118.  
 $C_{16}H_{16}OBr_2$   $\beta\gamma$ -Dibromophenyl-*p*-methoxyphenylpropanes. (INGOLD and PIGGOTT), 2386.  
 $C_{16}H_{14}Cl_2S$   $\beta\beta'$ -Dichloro- $\beta\beta'$ -diphenyldiethyl sulphid $\dot{e}$  (POPE and SMITH), 1168.  
 $C_{16}H_{17}ON$  Acetyl derivative of dibenzylamine (SHORT and SMITH), 1806.  
 $C_{16}H_{15}ON$  Ethyl  $\alpha$ -cyano- $\gamma$ -phenylglutaconate (INGOLD, PERREN, and THORPE), 1782.  
 $C_{16}H_{15}O_2N$  *p*-Nitroso- $\beta$ -phenoxydiethylaniline (CLEMO and PERKIN), 645.  
 $C_{16}H_{18}O_2S_2$  4:4'-Dimethoxydi-*m*-tolyl disulphide (STEWART), 2553.  
 $C_{16}H_{13}ON$  Anil of *cyclohexanespiro-cyclopentane-3:4-dione* (KON), 523.  
 $C_{16}H_{16}NI$  2-*p*-Dimethylaminostyrylpyridine methiodide (MILLS and POPE), 946.  
 $C_{16}H_{15}O_2N_2$  *N*-Ethyl- $\omega$ -imide of  $\alpha\alpha'$ -dicyano- $\alpha$ -ethylcyclohexane-1:1-diacetic acid (KON and THORPE), 1802.  
 $C_{16}H_{13}ON_2$  Substance, from methylation of the  $\omega$ -imide of  $\alpha\alpha'$ -dicyanocyclohexane-1:1-diacetic acid (KON and THORPE), 1801.  
 $C_{16}H_{18}O_6S$  Hexadecanesulphonic acid, preparation and properties of (NOBBS), 2162.

## 16 IV

- $C_{16}H_{10}ONCl$  2-Chloroacetylaminanthraquinone (BARNETT and COOK), 796.  
 $C_{16}H_{11}ONSe$  Cyanoselenium dibenzoylmethane (MORGAN, DREW, and BARKER), 2468.  
 $C_{16}H_{13}N_2IS$  Dibenzothiazolylmethane methiodide (MILLS), 465.  
 $C_{16}H_{15}ON_2S$  Substance, from thioethylene glycol and phenylcarbimide (BENNETT), 2146.  
 $C_{16}H_{11}Cl_2As_2Pt$  Platinum bis- $\beta$ -chlorovinylbis- $\beta\beta\beta'$ -trichlorotrivinylarsine (MANN and POPE), 1758.  
 $C_{16}H_{20}O_2Cl_4Te$  Tellurium bispivalylacetone dichloride (MORGAN and DREW), 933.

## 16 V

- $C_{16}H_{11}O_2Cl_{11}As_2Pt$  Bis- $\beta\beta'$ -dichlorodivinylchloroarsinebis- $\beta\beta'$ -dichlorodivinylhydroxyarsine platinumchloride (MANN and POPE), 1759.

**C<sub>17</sub> Group.**

- $C_{17}H_{16}O$  2-Hydroxybenzanthrone (PERKIN and SPENCER), 477.  
 $C_{17}H_{15}N$  1-Styrylisoquinoline (MILLS and SMITH), 2732.  
 $C_{17}H_{16}O$  3:2-Dihydroxydistyryl ketone (+ H<sub>2</sub>O) (BUCK and HEILBRON), 1097.  
 $C_{17}H_{17}O$  3-Ethoxy-2-phenylbenzopyrylium hydroxide, salts of (PRATT and ROBINSON), 1530.  

*p*-Methoxybenzylcinnamic acids (INGOLD and PIGGOTT), 2386.  
 Phenyl 2-hydroxy- $\beta$ -ethoxystyryl ketone (PRATT and ROBINSON), 1530.  
 $C_{17}H_{17}O$  7-Hydroxy-3-ethoxy-2-phenylbenzopyrylium hydroxide, salts of (PRATT and ROBINSON), 1533.  
 $C_{17}H_{15}O_2$  Benzoyl derivative of *cyclohexanespiro-cyclopentane-3:4-dione* (KON), 523.  
 $C_{17}H_{18}N_2$  2:8-Tetramethyldiaminoacridine (MOUNGILL), 1538.  
 $C_{17}H_{20}O$  Benzylidene-*dl*-piperitone (READ and SMITH), 574.  
 $C_{17}H_{20}O$  Benzyl-*p*-menthenol (READ and SMITH), 581.

## 17 III

- $C_{17}H_8O_4N$  1:2-Dioxanthraquinonequinolines, aminocobaltic salts (MORGAN and SMITH), 168.
- $C_{17}H_8O_4N$  6:7-Methylenedioxy-2:3(3-ketoindeno)(1:2)-quinoline (ARMIT and ROBINSON), 835.
- $C_{17}H_{12}ON$  2-Aminobenzanthrone (PERKIN and SPENCER), 480.
- $C_{17}H_8O_4N$  6:7-Methylenedioxy-2:3-indenoquinolines, and their salts (ARMIT and ROBINSON), 832.
- $C_{17}H_{11}O_2N$  2:5-Dipiperonyloxazole (GREENE and ROBINSON), 2188.
- $C_{17}H_{11}O_4N$  6'-Nitro-3':4'-methylenedioxy-2-benzylidene-1-hydrindone (ARMIT and ROBINSON), 830.
- Substance, from benzoylmethylenedioxymandelonitrile and sodium ethoxide (GREENE and ROBINSON), 2187.
- $C_{17}H_{11}O_2N$  *m*-Nitrobenzene-1-azo-2-oxy-3-naphthoic acid, and its cobalt-amine salt (MORGAN and SMITH), 2873.
- $C_{17}H_{11}O_2N$  Hydroxy- $\alpha$ -naphthylidenenitroanilines (MORGAN and REEVES), 4.
- $C_{17}H_{13}O_4Cl$  Hydroxy-2-styrylbenzopyrylium chlorides, and their salts (BUCK and HEILBRON), 1204.
- $C_{17}H_{13}O_4N$  6'-Amino-3':4'-methylenedioxy-2-benzylidene-1-hydrindone (ARMIT and ROBINSON), 331.
- $C_{17}H_{13}O_4Cl$  Dihydroxy-2-styrylbenzopyrylium chlorides (BUCK and HEILBRON), 1207.
- $C_{17}H_{13}O_4Cl$  2':4':7-Trihydroxy-2-styrylbenzopyrylium chloride (BUCK and HEILBRON), 1208.
- $C_{17}H_{13}NS$  4-Phenyl-2-styrylthiazole (MILLS and SMITH), 2734.
- $C_{17}H_{14}S_2$  2-Ethylbenzothiazolénylbenzothiazolylmethane (MILLS), 464.
- $C_{17}H_{14}O_2N_2$  Acetonaphthalide- $\alpha$ -pyridinium hydroxides, salts of (BARNETT and COOK), 795.
- $C_{17}H_{17}O_2N_2$  *iso*-Nitrosomalonanilide (RENDALL and WHITELEY), 2115.
- $C_{17}H_{18}O_2N_4$  2:4-Dinitrobenzaldoxime-*N*-*p*-diethylaminophenyl ether (BARROW, GRIFFITHS, and BLOOM), 1715.
- $C_{17}H_{18}O_4N$  Ethyl 2-carboxyindole-1:3-diacetate (KERMACK, PERKIN, and ROBINSON), 1893.
- $C_{17}H_{20}O_2N_2$  Nitrobenzoyl-*dl*-piperitone- $\alpha$ -oximes (READ, SMITH, and BENTIVOGGIO), 591.
- $C_{17}H_{20}O_4N_4$  3:3'-Dinitro-4:4'-tetramethyldiaminodiphenylmethane (MCGILL), 1507.

## 17 IV

- $C_{17}H_{11}ONCl$  2:6-Dichlorotoluene-4-azo-*B*-naphthol (DAVIES), 813.
- $C_{17}H_{17}O_2NCl$   $\beta$ -Naphthyl acetate  $\alpha$ -pyridinium chloride (+  $H_2O$ ) (BARNETT and COOK), 787.
- $C_{17}H_{17}O_2NBr$  Bromomalonmethylbromoanilide (WEST), 2199.
- $C_{17}H_{17}N_2IS_2$  Dibenzoethiazolylmethane ethiodide (MILLS), 464.
- 2:2'-Dimethylthiocyanine iodide (MILLS), 465.
- $C_{17}H_{17}O_4N_2S$  Quindoline methosulphate (ARMIT and ROBINSON), 836.
- $C_{17}H_{17}O_4N_2Cl$  Chloromalonmethylanilide (WEST), 2199.
- $C_{17}H_{17}O_4N_2Br$  Bromomalonmethylanilide (WEST), 2199.
- $C_{17}H_{17}ONCl$  *Py-N*-Methyl-*Ind-N*-propylharmin chloride (KERMACK, PERKIN, and ROBINSON), 1894.
- Py-N*-Propyl-*Ind-N*-methylharmin chloride (KERMACK, PERKIN, and ROBINSON), 1894.

**C<sub>18</sub> Group.**

- C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>** Lactone of hydroxybenzanthronecarboxylic acid (BRADSHAW and PERKIN), 913.  
**C<sub>18</sub>H<sub>10</sub>O<sub>4</sub>** Hydroxybenzanthronecarboxylic acid, and its salts (BRADSHAW and PERKIN), 913.  
**C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>** 3':4'-Methylenedioxy-2-hydroxydistyryl ketone (BUCK and HEILBRON), 1099.  
**C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>** Methyl 2-methoxyanthraquinone-1-glyoxylate (BRADSHAW and PERKIN), 917.  
**C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>** Methoxy-2-hydroxydistyryl ketones (BUCK and HEILBRON), 1098.  
**C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>** Oleic acid, sodium salt, ultra-filtration of solutions of (McBAIN and JENKINS), 2325.

**18 III**

- C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>**  $\alpha\alpha'$ -Dicyanodibenzyl diketone, colouring matters from (DUFF and SEN), 2663.  
**C<sub>18</sub>H<sub>11</sub>Cl<sub>3</sub>Bi** Tri-*p*-chlorophenylbismuthine (CHALLENGER and RIDGWAY), 108.  
**C<sub>18</sub>H<sub>11</sub>Cl<sub>2</sub>Bi** Tri-*p*-chlorophenylbismuthine dichloride (CHALLENGER and RIDGWAY), 109.  
**C<sub>18</sub>H<sub>11</sub>Br<sub>3</sub>Bi** Tri-*p*-bromophenylbismuthine (CHALLENGER and RIDGWAY), 111.  
**C<sub>18</sub>H<sub>11</sub>Br<sub>2</sub>Bi** Tri-*p*-bromophenylbismuthine dibromide (CHALLENGER and RIDGWAY), 111.  
**C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>N** Anhydro-6:7-methylenedioxy-2:3-indeno(2:1)-quinoline methohydroxide (ARMIT and ROBINSON), 834.  
**C<sub>18</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>** Carbazole-3-azoresorcinol (MORGAN and READ), 2713.  
**C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>** Nitrophenylaminohydroxy- $\alpha$ -naphthylacetonitriles (MORGAN and REEVES), 4.  
**C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>Cl** 3':4'-Methylenedioxy-2-styrylbenzopyrylium chloride (BUCK and HEILBRON), 1209.  
**C<sub>18</sub>H<sub>11</sub>ON<sub>2</sub>** Phenylaminohydroxy- $\alpha$ -naphthylacetonitriles (MORGAN and REEVES), 4.  
**C<sub>18</sub>H<sub>11</sub>O<sub>11</sub>N<sub>4</sub>** Ethyl 4:6:4':6'-tetranitrodiphenate (CHRISTIE and KENNER), 619.  
**C<sub>18</sub>H<sub>11</sub>O<sub>2</sub>N** Ethyl 2:3-indeno(2:1)indolecarboxylate (PERKIN and TITLEY), 1568.  
**C<sub>18</sub>H<sub>11</sub>O<sub>2</sub>Cl** Methoxy-2-styrylbenzopyrylium chlorides, and their salts (BUCK and HEILBRON), 1209.  
**C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>Cl** 3'-Methoxy-4'-hydroxy-2-styrylbenzopyrylium chloride (BUCK and WILLIAMS), 1208.  
**C<sub>18</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>** Hydrazones of methyl 5-aldehydosalicylate (WAYNE and COHEN), 1026.  
**C<sub>18</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>** Ethyl carbazole-3-azooacetate (MORGAN and READ), 2714.  
**C<sub>18</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>** Ethyl 2-hydrindone-1-carboxylate *p*-nitrophenylhydrazones (PERKIN and TITLEY), 1569.  
**C<sub>18</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>** Ethyl 2-hydrindone-1-carboxylate phenylhydrazones (PERKIN and TITLEY), 1568.  
**C<sub>18</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>** *iso*-Nitrosomalonanilide *n*- and *iso*-propyl ethers (RENDALL and WHITELEY), 2116.  
**C<sub>18</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>** *iso*-Nitrosomalondibenzylamide methyl ether (RENDALL and WHITELEY), 2118.  
**C<sub>18</sub>H<sub>11</sub>ON** Base, and its salts, from aniline and acetaldehyde (MANN), 2179.  
**C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>N** Anilic acid from *cis*-1-methyl-1- $\alpha$ -hexylcyclopropane-2:3-dicarboxylic acid (BIRN and THORPE), 1829.

- $C_{16}H_{17}O_5N$  Ethyl  $\alpha$ -cyanomethanetetraacetate (INGOLD and NICKOLLS), 1646.  
Ethyl  $\beta$ -cyanoisopentane- $\alpha,\beta,\gamma,\delta$ -tetracarboxylate (INGOLD and NICKOLLS), 1647.

18 IV

- $C_{18}H_{11}O_4NS$  4-Phenyl-2-thiazolylphthalonylmethane (MILLS and SMITH), 2734.  
 $C_{18}H_{12}Cl_2Br_2Bi$  Tri-*p*-bromophenylbismuthine dichloride (CHALLENGER and RIDGWAY), 111.  
 $C_{18}H_{12}Cl_2Br_2Bi$  Tri-*p*-chlorophenylbismuthine dibromide (CHALLENGER and RIDGWAY), 109.  
 $C_{18}H_{11}ON_2Cl_2$  4':4''-Dichloro-2:4-bisbenzeneazophenol (CHATTAWAY and HILL), 2758.  
 $C_{18}H_{11}ON_2Br_2$  4':4''-Dibromo-2:4-bisbenzeneazophenol (CHATTAWAY and HILL), 2759.  
 $C_{18}H_{11}ON_2I_2$  4':4''-Diiodo-2:4-bisbenzeneazophenol (CHATTAWAY and HILL), 2759.  
 $C_{18}H_{11}ON_2Cl$  Chlorobenzeneazobenzeneazophenols (CHATTAWAY and HILL), 2759.  
 $C_{18}H_{11}ON_2Br$  Bromobenzeneazobenzeneazophenols (CHATTAWAY and HILL), 2759.  
 $C_{18}H_{11}ON_2I$  Iodobenzeneazobenzeneazophenols (CHATTAWAY and HILL), 2760.  
 $C_{18}H_{13}O_{11}N_2Pb_4$  Lead *m*-nitrophenoxide (GODDARD and WARD), 264.  
 $C_{18}H_{13}ON_2Cl$  4-Chloroacetylaminonaphthalene-1-azobenzene (BARNETT and COOK), 795.  
 $C_{18}H_{11}ON_2S$  2-Amino-8-thiol-10-phenylphenazonium hydroxide (WATSON and DUTT), 1941.  
 $C_{18}H_{11}OF_2Bi$  Triphenylbismuthine difluoride (CHALLENGER and WILKINSON), 96.  
 $C_{18}H_{13}O_2N_2S_2$  Diethylsulphine-(bis)-*p*-toluenesulphonylimine (MANN and POPE), 1054.

$C_{19}$  Group.

- $C_{19}H_{15}O_3$  Ethoxybenzanthrone, and its salts (PERRIN and SPENCER), 477.  
 $C_{19}H_{17}O_4$  3':4'-Dimethoxy-2-hydroxydistyryl ketone (BUCK and HEILBRON), 1099.  
 $C_{19}H_{21}O_5$  Trimethoxy- $\beta$ -gambier-catechincarboxylic acid (NIERENSTEIN), 28.  
 $C_{19}H_{17}O_5$  4:6:3':4'-Tetramethoxy-3-phenylchroman (NIERENSTEIN), 612.  
 $C_{19}H_{17}O_5$  2-Hydroxy-3:4-dimethoxyphenyl  $\beta$ -veratrylethyl ketone (CRABTREE and ROBINSON), 1038.  
 $C_{19}H_{19}O_5$  Menthyl phenoxymalonate (SHIMOMURA and COHEN), 2054.

19 III

- $C_{19}H_{15}O_4N_2$  Alizarin pyridiniumnitrolobetaines (BARNETT and COOK), 1388.  
 $C_{19}H_{17}O_4N_2$  2-Acetylaminobenzanthrone (PERRIN and SPENCER), 480.  
 $C_{19}H_{17}O_4N_2$  9-Nitroanthranil-10-pyridinium hydroxide, salts of (BARNETT, COOK, and GRAINGER), 2064.  
 $C_{19}H_{17}O_4N$  Anhydro-6:7-methylenedioxy-2:3(3-methylindeno)(2:1)-quinoline methohydroxide (ARMIT and ROBINSON), 834.  
 $C_{19}H_{17}O_4N$  9-Hydroxyanthranil-10-pyridinium hydroxide, salts of (BARNETT, COOK, and GRAINGER), 2065.  
 $N$ -Phenylbenziminom-*m*-hydroxyphenyl ether, and its hydrochloride (CHAPMAN), 1676.



- $C_{11}H_{11}OS_3$  *pp'*-Trithioltriphenylcarbinol (WATSON and DUTT), 1940.
- $C_{11}H_{11}O_2N_2$  Quinoxaline derivative of *ac*-1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic lactone (KON, STEVENSON, and THORPE), 661.
- Xanthorocellin (FORSTER and SAVILLE), 821.
- $C_{15}H_{11}O_2N_2$   $\alpha$ -Benzoylamino- $\beta$ -[6-methoxyindolyl(3)]-acrylic acid (KERNACK, PERKIN, and ROBINSON), 1883.
- $C_{11}H_{11}O_2Cl$  3':4'-Dimethoxy-2-styrylbenzopyrylium chloride (BUCK and HEILBRON), 1210.
- $C_{15}H_{11}O_2N_2$  Ethyl 1-methyl-2-hydrindone-1-carboxylate *p*-nitrophenylhydrazones (PERKIN and TILLEY), 1569.
- $C_{15}H_{11}O_2N_2$  *p*-Nitrophenylhydrazones of *ac*-1-keto-2-hydroxy-3-methyltetrahydronaphthalene-3-acetic lactone (KON, STEVENSON, and THORPE), 662.
- $C_{11}H_{10}O_2N_2$  Acetyldiphenylamine- $\alpha$ -pyridinium hydroxide, salts of (BARNETT and COOK), 796.
- $C_{11}H_{11}N_2Cl$  Substance, from thiocarbanilide and chloropierin (RAY and DAS), 327.
- $C_{15}H_{11}ON$   $\beta$ -Naphthoxyethylmethylaniline (CLEMO and PERKIN), 649.
- $C_{15}H_{11}O_2N$  Anilic acid from *cis*-1-benzyl-1-methylcyclopropane-2:3-dicarboxylic acid (BIRCH and THORPE), 1833.
- $C_{15}H_{12}O_2N_2$  Quinoxaline derivative of methylcyclopentanespirocyclopentane-3:4-dione-2:5-dicarboxylate (DICKENS, KON, and THORPE), 1502.
- $C_{15}H_{11}O_2N_2$  *iso*Nitrosomalonanilide *n*-butyl ether (RENDALL and WHITELEY), 2116.
- iso*Nitrosomalondibenzylamide ethyl ether (RENDALL and WHITELEY), 2118.
- $C_{15}H_{11}O_2Cl$  2-Chloro-4:6:3':4'-tetramethoxy-3-phenylchroman (NIERENSTEIN), 611.
- $C_{15}H_{11}O_2Br$  3-Bromo-4:6:3':4'-tetramethoxy-3-phenylchroman (NIERENSTEIN), 612.
- $C_{15}H_{11}O_2Br$  3-Bromo-2-hydroxy-4:6:3':4'-tetramethoxy-3-phenylchroman (NIERENSTEIN), 609.
- $C_{15}H_{11}ON$  Cinchonidine, salt of tropic acid with (KING and PALMER), 2585.
- Cinchotoxine, salt of tropic acid with (KING and PALMER), 2584.
- $C_{15}H_{11}ON$  Hydrocinchonidine, salts of tropic acid with (KING and PALMER), 2585.
- Hydrocinchonine, salts of tropic acid with (KING and PALMER), 2585.

## 19 IV

- $C_{11}H_{11}O_2NBr$  Phenobetaine of bromoalazarinpyridinium bromide (BARNETT and COOK), 1385.
- $C_{11}H_{11}O_2NBr_2$  Bromoalazarinpyridinium bromide (+14H<sub>2</sub>O) (BARNETT and COOK), 1385.
- $C_{15}H_{13}O_2NS$  Catecholsulphamphthalein (DUTT), 2392.
- Resorcinolsulphamphthalein (DUTT), 2391.
- $C_{15}H_{13}O_2NS$  Hydroxyquinolsulphamphthalein (DUTT), 2392.
- Phloroglucinolsulphamphthalein (DUTT), 2391.
- $C_{15}H_{13}O_2NS$  1:2:4:5-Tetrahydroxybenzenesulphamphthalein (DUTT), 2392.
- $C_{15}H_{11}O_2NS$  2:2'-Iminophenolsulphamphthalein (DUTT), 2393.
- $C_{15}H_{13}ON_2Br$  Bromobenzeneazop-toluenesazophenols (CHAFFAWAY and HILL), 2760.
- $C_{15}H_{11}O_2N_2S_2$  Diphenylbisazo-2-hydroxy-7-naphthyl xanthate (WATSON and DUTT), 2417.
- $C_{15}H_{13}O_2NS$  Phenolsulphamphthalein, and its sodium salt (DUTT), 2390.

- $C_{19}H_{11}ON_2S_2$  Ethyl 4-benzeneazo-1-naphthylxanthate (WATSON and DUTT), 1940.  
 $C_{19}H_{11}O_2N_2S$  4:4'-Diamino-2:2'-iminophenylsulphamphthalein (DUTT), 2392.  
 $C_{19}H_{17}ON_4Cl$  *p*-Chloroacetylaminoozobenzene pyridinium chloride (BARNETT and COOK), 795.  
 $C_{18}H_{17}N_7IS_2$  2:2'-Diethylthiocyanine iodide (MILLS), 461.  
 $C_{17}H_{13}N_2IS$  4-Phenylthiazole-2-aldehyde *p*-dimethylaminoanil methiodide (MILLS and SMITH), 2735.  
 $C_{15}H_{21}O_2NBr$  1-Bromo-2-salicylidene-3:5:6-triacetyl glucosamine (IRVINE and EARL), 2375.

### C<sub>20</sub> Group.

- $C_{20}H_{14}O_4$  Hydroxybenzanthronecarboxylic acid dimethyl ether (BRADSHAW and PERKIN), 914.  
 $C_{20}H_{12}N_4$  *aa'*-Dicyano-2:3-dibenzyl-5:6-dihydropyrazine (DUTT and SEN), 2661.  
 $C_{20}H_{26}O_{12}$  Acertannin (PERKIN and UYEDA), 68.  
 $C_{20}H_{24}O_6$  3:4:6:3':4':Pentamethoxy-3-phenylchroman (NIERENSTEIN), 613.  
 $C_{20}H_{24}O_7$  2-Hydroxy-3:4:6:3':4':pentamethoxy-3-phenylchroman (NIERENSTEIN), 610.  
 $C_{20}H_{26}O_4$  Ethyl thapsate (CARMICHAEL), 2548.

### 20 III

- $C_{20}H_{11}O_2S_2$  Dithiolfluorescein (WATSON and DUTT), 1942.  
 $C_{20}H_{11}O_2N_4$  4-Nitronaphthaleneazo-4-nitro-*a*-naphthol (MUKERJI), 2881.  
 $C_{20}H_{11}O_4N_2$  Diamide of *aa'*-dicyano-*B*-benzylglutaric acid (STEVENS and THORPE), 1720.  
 $C_{20}H_{12}O_2S_2$  1:1'-Dihydroxy-5:5'-dinaphthyl disulphide (WATSON and DUTT), 2416.  
 $C_{20}H_{12}O_2S_3$  Di-*a*-naphthol trisulphide (WATSON and DUTT), 2418.  
 $C_{20}H_{11}O_2S_4$  Benzenedi-*a*-thiobenzoic acid, and its sodium salt (SMILES and GRAHAM), 2508.  
 $C_{20}H_{11}O_2N_4$  2:4-Dinitrobenzilmonophenylhydrazone (BISHOP and BRADY), 2369.  
 $C_{20}H_{11}ClTI$  Thallium di-*a*-naphthyl chloride (D. and A. E. GODDARD), 261.  
 $C_{20}H_{11}BrTI$  Thallium di-*a*-naphthyl bromide (D. and A. E. GODDARD), 258.  
 $C_{20}H_{11}O_4Se_4$  Selenium benzoylacetone (MORGAN, DREW, and BARKER), 2455.  
 $C_{20}H_{11}O_4Se_3$  *cyclo*Triselenium bisbenzoylacetone (MORGAN, DREW, and BARKER), 2454.  
 $C_{20}H_{18}O_4N_2$  Methylxanthorocellin (FORSTER and SAVILLE), 822.  
 $C_{20}H_{11}O_4Se$  Selenium bisbenzoylacetone (MORGAN, DREW, and BARKER), 2459.  
 $C_{20}H_{11}O_4Se_2$  Diselenium bisbenzoylacetone (MORGAN, DREW, and BARKER), 2457.  
 $C_{20}H_{20}O_4N_2$  Anhydriporocellin (FORSTER and SAVILLE), 821.  
 $C_{20}H_{11}O_2N_2$  Ethyl *N*-ethylcarbazole-3-azooacetate (MORGAN and READ), 2716.  
 $C_{20}H_{11}NI$  1-*p*-Dimethylaminostyrylisoquinoline methiodide (MILLS and SMITH), 2733.  
 $C_{20}H_{22}O_2N_2$  Picrorocellin, constitution of (FORSTER and SAVILLE), 816.

- $C_{25}H_{20}O_2Cl$  2-Chloro-3:4:6:3':4'-pentamethoxy-3-phenylchroman (NIERENSTEIN), 618.  
 $C_{20}H_{22}ON_2$  Base, from *p*-toluidine and acetaldehyde (MANN), 2182.  
 $C_{20}H_{20}O_2N_2$  Quinotoxine, salts of tropic acid with (KING and PALMER), 2584.  
 $C_{20}H_{20}O_2N_2$  Dip-toluidide of  $\alpha$ -hydroxy- $\beta$ -methylglutaric acid (INGOLD), 2689.  
 $C_{10}H_{11}O_2N_2$  Dip-toluidides of  $\alpha\alpha$ -dihydroxy- $\beta$ -methylglutaric acids (INGOLD), 2691.  
 $C_{10}H_{21}O_2N$  2-Salicylidene-3:5:6-triacetyl-1-methyl glucoseamine (IRVINE and EARL), 2379.  
 $C_{10}H_{19}O_2N_2$  Hydroquinidine, salt of tropic acid with (KING and PALMER), 2582.  
 Hydroquinine, salts of, with tropic acid (KING and PALMER), 2582.  
 $C_{10}H_{17}O_{11}N$  Amygdalin, biase from (HAWORTH and LEITCH), 1921.  
 $C_{20}H_{21}O_5N$  Ethyl  $\omega$ -cyano- $\omega''$ -dicarboxymethanetriacetate (INGOLD and FERRES), 1418.

## 20 IV

- $C_{20}H_{11}O_4Cl_2Te$  Tellurium bisbenzoylacetone dichloride (MORGAN and DREW), 830.  
 $C_{20}H_{11}O_4FeCl_4$  7:5:6'-Trimethoxy-2-methyl-3:4-indeno(2':1')-benzopyrylium ferrichloride (CRABTREE and ROBINSON), 1036.  
 $C_{20}H_{11}O_4FeCl_4$  Isoflametin ferrichloride tetramethyl ether (CRABTREE and ROBINSON), 1039.  
 $C_{10}H_{11}O_4NS$  6:7-Methylenedioxy-2:3(3'-ketoindeno(1:2)-quinoline methosulphate (AKMIT and ROBINSON), 836.  
 $C_{20}H_{11}N_4IS$  4-Phenyl-2-*p*-dimethyl aminostyrylthiazole methiodide (MILLS and SMITH), 2735.  
 $C_{20}H_{21}N_4IS_2$  Methyl-diethylthiocyanine iodides (MILLS), 461; (MILLS and BRANCHOLTZ), 1493.  
 $C_{20}H_{21}O_4Se_2Cu$  Copper selenium *o*-bisacetylacetone (MORGAN, DREW, and BARKER), 2451.

 $C_{21}$  Group.

- $C_{21}H_{15}O_4$  3-Phenoxy-2-phenylbenzopyrylium hydroxide, ferrichloride of (PRAIT and ROBINSON), 1582.  
 Phenyl 2-hydroxy- $\beta$ -phenoxy-styryl ketone (PRAIT and ROBINSON), 1581.  
 $C_{21}H_{15}O_4$  7-Hydroxy-3-phenoxy-2-phenylbenzopyrylium hydroxide, ferrichloride of (PRAIT and ROBINSON), 1581.  
 $C_{21}H_{15}O_6$  Pentamethoxy  $\beta$ -gambier-catechincarboxylic acid (NIERENSTEIN), 28.  
 $C_{21}H_{15}O_6$  2-Hydroxy-1:6:3':4'-tetramethoxy-3-ethoxy-3-phenylchroman (NIERENSTEIN), 619.

## 21 III

- $C_{21}H_{11}O_2N_2$  2-Chloroacetylaminonanthraquinone pyridinium hydroxide salts of (BAENETT and COOK), 796.  
 $C_{21}H_{11}O_2N$  4-Dimethylamino-trihydroxy-9-phenylfluorones (MCKEEN), 350.  
 $C_{21}H_{21}NBr$  Cinnamylidenequinaldine ethobromide (MILLS and HAMER), 2013.  
 $C_{21}H_{21}NI$  Cinnamylidenequinaldine ethiodide (MILLS and HAMER), 2012.  
 $C_{21}H_{21}O_2N_2$  Methylanthropicrocillin (FORSTER and SAVILLE), 821.  
 $C_{21}H_{14}O_2N_2$  Dianilide of *trans*-3:3-dimethylcyclopropane 1:2 dicarboxylic acid (DESHAPANDE and THORPE), 1437.

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## 21 III-22 III

$C_{11}H_{10}O_2N_2$  Dianilide of 3:3-diethylcyclopropanol-1:2-dicarboxylic acid (DESHAPANDE and THORPE), 1441.

$C_{21}H_{28}O_2N_2$  Ethylhydrocupreine, salt of tropic acid with (KING and PALMER), 2583.

Ethylhydrocupreidine, salts of tropic acid with (KING and PALMER), 2583.

## 21 IV

$C_{21}H_{17}O_2NS$  Orçinoisulphamphthalein (DUTT), 2391.

$C_{21}H_{19}O_{11}N_2Pb_4$  Lead 4-nitro-*o*-tolylxide (GONNARD and WARD), 265.

$C_{21}H_{19}N_2IS$  4-Phenyl-3-methyl-2-thiazolanyl-4-quinolylmethane methiodide (MILLS and SMITH), 2736.

$C_{21}H_{21}O_2NS_2$  Dibenzylsulphine-*p*-toluenesulphonylimine (MANN and POPE), 1053.

$C_{21}H_{21}O_2FeCl_4$  7:5':6'-Trimethoxy-2-ethyl-3:4-indeno(2':1')-benzopyrylium ferrichloride (CHARTREE and ROBINSON), 1937.

$C_{21}H_{21}O_2FeCl_4$  7:8:5':6'-Tetramethoxy-2-methyl-3:4-indeno(2':1')-benzopyrylium ferrichloride (CHARTREE and ROBINSON), 1041.

$C_{21}H_{21}N_2IS$  21:1'-Diethylthioisocyanine iodide (BRAUNHOLTZ and MILLS), 2006.

1':6'-Dimethyl-2-ethylthioisocyanine iodide (BRAUNHOLTZ and MILLS), 2007.

$C_{21}H_{21}N_2IS_2$  2:2'-Diethylcarbothiocyanine iodide (MILLS), 462; (MILLS and BRAUNHOLTZ), 1493.

$C_{21}H_{21}ONCl_3$  2:4:5:7-Tetra-amino-4'-dimethylamino-9-phenylfluorone trichloride (MUKERJI), 550.

## $C_{22}$ Group.

$C_{22}H_{18}O_4$  Methylenedioxybenzoylbenzoin (GREENE and ROBINSON), 2190.  
Resorcinolphenylsuccinein (LAPWORTH and McRAE), 2723.

$C_{22}H_{18}N_4$  Carbazole-3-azo- $\beta$ -naphthylamine (MORGAN and READ), 2714.

$C_{22}H_{18}O_4$  4'-Methoxybenzoylbenzoin (GREENE and ROBINSON), 2189.

$C_{22}H_{22}O_3$  Phenolcamphorein anhydride (SINGH, RAI, and LAL), 1425.

$C_{22}H_{22}O_3$  Quinolcamphorein (SINGH, RAI, and LAL), 1427.

Resorcinolcamphorein (KRISHNA), 255; (SIRCAR and DUTT), 1284.

$C_{22}H_{22}O_3$  Phloroglucinolcamphorein (SIRCAR and DUTT), 1288; (SINGH, RAI, and LAL), 1428.

Pyrogallolcamphorein (SINGH, RAI, and LAL), 1428.

$C_{22}H_{20}O_4$  Phenolcamphorein (KRISHNA), 254; (SINGH, RAI, and LAL), 1425.

$C_{22}H_{20}O_4$  Catecholcamphorein (SINGH, RAI, and LAL), 1427.

$C_{22}H_{24}O_6$  2-Acetoxy-3:4:5:3':4'-pentamethoxy 3-phenylchroman (NIERENSTEIN), 610.

Pentamethoxymethyl  $\beta$ -gambier-catechin-carboxylate (NIERENSTEIN), 27.

$C_{22}H_{36}O_4$  Capsularin (SAHA and CHOUDHURY), 1044.

$C_{22}H_{40}O_2$  Behenic acid, sodium salt, properties of solutions of (FLECKER and TAYLOR), 1101.

## 22 III

$C_{22}H_{18}O_2N_2$  2:4-Dipthaliminophenol (MUKERJI), 549.

$C_{22}H_{18}O_2Br_4$  Phenylsuccinyleosin (LAPWORTH and McRAE), 2724.

$C_{22}H_{18}O_2N_4$  4:6-Dipthaliminoresorcinol (MUKERJI), 549.

$C_{22}H_{18}O_2N_2$  2:3-Dipiperonylquinoxaline (GREENE and ROBINSON), 2194.

$C_{22}H_{18}ON_2$  Carbazole-3-azo-3-naphthol (MORGAN and READ), 2713.

- $C_{21}H_{11}O_2N$  6'-Nitro-3':4'-methylenedioxybenzoylbenzoin (GREENE and ROBINSON), 2190.  
 $C_{21}H_{17}Cl_4Bi$  Diphenyl-naphthylbismuthine dichloride (CHALLENGER and WILKINSON), 102.  
 $C_{21}H_{18}O_4Br_4$  Tetrabromoresorcinolcamphorein (SIRCAR and DUTT), 1285; (SINGH, RAI, and LAL), 1429.  
 $C_{21}H_{16}ON_4$  2-Hydrindonecarboxylic acid phenylhydrazide phenylhydrazone (PERKIN and TITLEY), 1568.  
 $C_{21}H_{18}O_4Br_4$  Tetrabromophenolcamphorein (KRISHNA), 255.  
 $C_{21}H_{18}O_2N$  *m*-Aminophenolcamphorein (SIRCAR and DUTT), 1286.  
 $C_{21}H_{18}O_4N_4$  *cyclo*Hexanespirocyclopentane-3:4-dione osazone (KON), 523.  
 $C_{21}H_{14}N_2S_2$  Benzenedi-*p*-thiodimethylaniline (SMILES and GRAHAM), 2510.  
 $C_{21}H_{18}N_2Cl$  Substance, from *s*-ditolylthiocarbamide and chloropierin (RAY and DAS), 327.  
 $C_{21}H_{18}O_2N_2$  *m*-Phenylenediaminecamphorein (SIRCAR and DUTT), 1286.  
 $C_{21}H_{18}O_2N_2$  Dimethylpicrorocellin (FORSTER and SAVILLE), 820.  
 $C_{21}H_{18}N_2S_2$  *p*-Xylenedi-*p*-thiodimethylaniline (SMILES and GRAHAM), 2510.  
 $C_{21}H_{20}O_2N$  2-Salicylidene-3:5:6-triacetyl-1-ethyl glucosamine (IRVINE and EARD), 2380.  
 $C_{21}H_{20}O_2S_2$  88'-Diphenoxy- $\alpha\alpha'$ -dimethyldiisobutyl disulphide (POPE and SMITH), 1168.  
 $C_{21}H_{20}O_4N_2$  Ethyl 2:4-dicyano-2:4-dicarboxycyclobutane-1:3-di-*a*-propiolate (ISGOLD, PERREN, and THORPE), 1787.

## 22 IV

- $C_{21}H_{11}O_2N_4P$  Ethyltriphenylphosphineglyoxylate-azine, reactions of (BRAUNHOLZ), 304.  
 $C_{21}H_{11}O_4NS$  Trimethyl derivative of phenolsulphamphthalein (DUTT), 2390.  
 $C_{21}H_{18}N_2IS$  5-Methyl-2:4'-diethylthioisocyanine iodide (BRAUNHOLZ and MILLS), 2007.  
 5:1'-6'-Trimethyl-2-ethylthioisocyanine iodide (BRAUNHOLZ and MILLS), 2007.

 $C_{22}$  Group.

- $C_{22}H_{16}O_2$  5:5-Diketo-7:7-dimethyl-5:5-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 569.  
 $C_{22}H_{18}O_2$  Benzoylpiperoin (GREENE and ROBINSON), 2187.  
 $C_{22}H_{18}O$  7:7-Dimethyl- $\alpha$ -dinaphthaxanthen, oxidation of (SEN-GUPTA and TUCKER), 569.  
 $C_{22}H_{18}O_2$  5:9-Dihydroxy-7:7-dimethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 561.  
 $C_{22}H_{18}O_2$  5:9-Dimethoxy-7:7-dimethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 562.  
 $C_{22}H_{18}O_2$  Diisocumyloxydiphenylmethane (MACKENZIE), 1696.

## 23 III

- $C_{23}H_{11}O_2N$  6'-Nitro-3:4:3':4'-dimethylenetetraoxybenzoylbenzoin (GREENE and ROBINSON), 2192.  
 $C_{23}H_{17}O_2N$  Benzoyl-3-benzoyloxy-4-methoxymandelonitrile (GREENE and ROBINSON), 2195.  
 $C_{23}H_{11}O_2N$  *p*-Methoxybenzylinnamanilides (ISGOLD and PERRY), 2387.  
 $C_{23}H_{11}O_4N$  *p*-Nitrobenzylidenebis-*p*-nitrobenzaldehydemethylhydrazone (BRADY and McHUGH), 1651.

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## 23 III-24 III

$C_{25}H_{31}O_2N_4$  4'4''-Tetramethyldiamino-2,5-dihydroxyfuchsones (McKENN), 551.

$C_{25}H_{30}O_2N_4$  Brucine, salts of di- and tetra-nitrophenic acids, with (CHRISTIE and KENNER), 617.

$C_{25}H_{35}O_4N$  Ethyl 2-cyano-2:4:4-tricarboxycyclobutane-1-acetate-3- $\alpha$ -propionate (KINGOLD, PERREN, and THORPE), 1788.

## 23 IV

$C_{25}H_{19}ON_4Cl$  4-Chloroacetylamino-naphthalene-1-azobenzene pyridinium chloride (BARNETT and COOK), 795.

$C_{25}H_{21}O_2NS$  Diacetyl derivative of phenolsulphamphthalein (DUTT), 2390.

$C_{25}H_{25}O_2N_4S$  4:4'-Tetramethyldiamino-2:2'-oxidophenylsulphamphthalein (DUTT), 2294.

$C_{25}H_{28}N_4IS_2$  5:5'-Dimethyl-2:2'-diethylcarbothiocyanine iodide (MILLS), 464.

## 23 V

$C_{25}H_{25}ON_4IS$  6'-Ethoxy-2:4'-diethylthioisocyanine iodide (BRAUNHOLTZ and MILLS), 2007.

## $C_{24}$ Group.

$C_{24}H_{18}N_4$  Aminophenanthranaphthazines (SIRCAR and DUTT), 1947.

$C_{24}H_{16}O_4$   $\beta\beta$ -Di-2- $\alpha$ -naphthaquinonylpropane (SEN-GUPTA and TUCKER), 561.

$C_{24}H_{14}N_4$  Diaminophenanthranaphthazines (SIRCAR and DUTT), 1946.  
 $\alpha\alpha'$ -Dicyano-2:3-dibenzylquinoxaline (DUTT and SEN), 2664.

$C_{24}H_{12}N_4$   $\alpha\alpha'$ -Dicyano-7-amino-2:3-dibenzylquinoxaline (DUTT and SEN), 2665.

$C_{24}H_{18}O_2$  5:6-Diketo-7-methyl-7-ethyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 563.

$C_{24}H_{18}O_4$   $\beta\beta$ -Di-2- $\alpha$ -naphthaquinonylbutane (SEN-GUPTA and TUCKER), 564.

$C_{24}H_{16}O$  7-Methyl-7-ethyl- $\alpha$ -dinaphthaxanthen, oxidation of (SEN-GUPTA and TUCKER), 563.

$C_{24}H_{16}O_2$  5:9-Dihydroxy-7-methyl-7-ethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 564.

5:6-Diketo-7-methyl-7- $n$ -propyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 566.

Fluoran derivative of camphoric anhydride (KRISHNA), 255.

$C_{24}H_{16}Pb$  Lead tetraphenyl, use of, in preparation of organo-metallic compounds (GODDARD, ASHLEY, and EVANS), 978.

$C_{24}H_{16}Sn$  Tin tetraphenyl, use of, in preparation of organo-metallic compounds (GODDARD, ASHLEY, and EVANS), 978; action of thallic chloride on (D. and A. E. GODDARD), 259.

$C_{24}H_{20}O_2$   $\alpha$ -Cresolcamphorein anhydride (SINGH, RAI, and LAI), 1427.

$C_{24}H_{20}O_4$   $\alpha$ -Cresolcamphorein (SINGH, RAI, and LAI), 1426.

Dimethyl ether of phenolcamphorein (KRISHNA), 254.

## 24 III

$C_{24}H_{11}O_4N_4$  Bromodinitrophenanthranaphthazine (SIRCAR and DUTT), 1948.

$C_{24}H_{11}N_4Br_2$  2:7-Dibromophenanthranaphthazine (SIRCAR and DUTT), 1947.

$C_{24}H_{15}O_2N_3$  Nitrophenanthranaphthazines (SIRCAR and DUTT), 1946.

$C_{24}H_{15}ON$  Hydroxyphenanthranaphthazines (SIRCAR and DUTT), 1947.

- $C_{24}H_{16}O_2N_2$  Dihydroxyphenanthranaphthazines (SIRCAR and DUTT), 1947.
- $C_{24}H_{16}O_2N$  2-Benzoylaminoanthracene (PERKIN and SPENCER), 481.
- $C_{24}H_{16}O_2N$  Hydroxybenzanthronecarboxyanilide (BRADSHAW and PERKIN), 913.
- $C_{24}H_{16}O_2N$  Nitro-derivative of 5:6-diketo-7:7-dimethyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 560.
- $C_{24}H_{16}O_2N_2$  2:6-Diketo-3:5-dibenzylidene-2:3:5:6-tetrahydro-*m-g*-benzobispyrrole (DAVIES and HICKOX), 2653.
- $C_{24}H_{16}O_2S_2$  Naphthalenedi-*m*-thiobenzoic acid (SMILES and GRAHAM), 2309.
- $C_{24}H_{16}O_2N$  Nitro-derivative of 5:6-diketo-7-methyl-7-ethyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 563.
- $C_{24}H_{16}OTl_2$  Thallium diphenyl oxide, and its salts (A. E. and D. GODDARD), 487.
- $C_{24}H_{16}O_2N_2$  Substance, from *m*-dinitrobenzene and hydroxymethoxydistyryl ketone (BUCK and HEILBRON), 1099.
- $C_{24}H_{16}O_2N_4$  2:7-Dinitrophenanthranaphthazine (SIRCAR and DUTT), 1945.
- $C_{24}H_{20}O_2N$   $\beta\beta'$ -Di-2-naphthoxydiethylamine (CLEMO and PERKIN), 616.
- $C_{24}H_{20}O_2Br_2$  Dibromo- $\alpha$ -cresolcamphorin (SINGH, RAI, and LAI), 1426.
- $C_{24}H_{20}O_2N$  Phenylurethane of benzyl *p*-menthenol (REAY and SMITH), 581.

## 24 IV

- $C_{24}H_{16}O_2N_2Br_2$  Dibromonitrophenanthranaphthazine (SIRCAR and DUTT), 1948.
- $C_{24}H_{16}O_2N_2Br$  5-Bromo-4-nitrophenanthranaphthazine (SIRCAR and DUTT), 1949.
- $C_{24}H_{16}O_2N_2S$  2:7-Dihydroxyphenanthranaphthazine-12-sulphonic acid (SIRCAR and DUTT), 1950.
- $C_{24}H_{16}O_2N_2S$  2-Aminophenanthranaphthazine-12-sulphonic acid, and its sodium salt (SIRCAR and DUTT), 1950.
- $C_{24}H_{16}O_2N_2Br$  Phenobetaine of alizarindipyridinium dibromide ( $+ H_2O$ ) (BARNEIT and COOK), 1387.
- Phenobetaine of hystazarindipyridinium dibromide (BARNEIT and COOK), 1388.
- Phenobetaine of quinizarin-2:3-dipyridinium dibromide (BARNEIT and COOK), 1384.
- $C_{24}H_{16}O_2N_2S$  2:7-Diaminophenanthranaphthazine-12-sulphonic acid, and its sodium salt (SIRCAR and DUTT), 1949.
- $C_{24}H_{16}O_2N_2Br_2$  Alizarindipyridinium dibromide (BARNEIT and COOK), 1386.
- Hystazarindipyridinium dibromide (BARNEIT and COOK), 1388.
- Quinizarin-2:3-dipyridinium dibromide (BARNEIT and COOK), 1381.
- $C_{24}H_{16}O_2N_2Br_4$  Alizarindipyridinium perbromide (BARNEIT and COOK), 1386.

## 24 V

- $C_{24}H_{16}ON_4IS$  6-Ethoxy-5-methyl-2:1'-diethylthiocyanine iodide (BRATSHOLTZ and MILLS), 2093.

 $C_{25}$  Group.

- $C_{25}H_{18}N_4$   $\alpha\alpha'$ -Dicyano-2:3-dibenzyl-8-methylquinoxaline (DUTT and SES), 2665.

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25 II—27 II

- $C_{25}H_{20}O_2$  5:6-Diketo-7:7-diethyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 565.  
 $C_{25}H_{20}O_4$  Di-2- $\alpha$ -naphthaquinonylpentanes (SEN-GUPTA and TUCKER), 565.  
 $C_{25}H_{22}O$  7:7-Diethyl- $\alpha$ -dinaphthaxanthen, oxidation of (SEN-GUPTA and TUCKER), 565.  
 7-Methyl-7-*n*-propyl- $\alpha$ -dinaphthaxanthen, oxidation of (SEN-GUPTA and TUCKER), 565.  
 $C_{25}H_{22}O_2$  8:9-Dihydroxy-7:7-diethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 565.  
 5:9-Dihydroxy-7-methyl-7-*n*-propyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 565.  
 $C_{25}H_{24}O_4$  Menthyl acetylmalonate (SHIMOMURA and COHEN), 2051.

## 25 III

- $C_{25}H_{19}O_2N$  Nitro-derivative of 5:6-diketo-7:7-diethyl-5:6-dihydro- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 565.  
 $C_{25}H_{21}N_2P$  Triphenylphosphinebenzaldehydeazine, and its reactions (BRAUNHOLTZ), 305.  
 $C_{25}H_{23}O_2N_2$  *trans*-1-Benzyl-1-methylcyclopropane-2:3-dicarboxylanilide (BIRCH and THORPE), 1832.

## 25 IV

- $C_{25}H_{21}N_2Br_2I$  Dibromo-1:1'-diethylazurine iodides (MOURGILL), 1510.

## 25 V

- $C_{25}H_{20}O_2N_2S_2Na_2$  Xylene cyanole FF (HICKMAN and LINSTEAD), 2504.

# $C_{26}$ Group.

- $C_{26}H_{24}O_2$  5:9-Dimethoxy-7-methyl-7-ethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 564.  
 $C_{26}H_{26}O_2$  Diacetyl derivative of phenolcamphorin (KRISHNA), 254.  
 $C_{26}H_{26}O_2$  Diethyl ether of phenolcamphorin (KRISHNA), 254.  
 $C_{26}H_{28}O_2$  Menthyl ethoxymethylenemalonate (SHIMOMURA and COHEN), 2055.

## 26 III

- $C_{26}H_{19}N_3Cl$  *iso*Quinoline-red (HARRIS and POPE), 1032.  
 $C_{26}H_{20}O_2N_4$  1:4-Diphenyl-3-*o*-nitrophenyl-2-*p*-nitrophenyl-1:3-dimethindiazidine (INGOLD and PIGGOTT), 2799.  
 $C_{26}H_{21}O_2N_4$  1:4-Diphenyl-3-*m*-nitrophenyl-2-*p*-hydroxyphenyl-1:3-dimethindiazidine (INGOLD and PIGGOTT), 2798.  
 $C_{26}H_{22}O_2N_2$  *m*-Dimethylaminophenocamphorin, hydrochloride of (SIRCAR and DUTTA), 1285.  
 $C_{26}H_{27}O_5N$  Ethyl 2-cyano-2:4:4-tricarboxycyclobutane-3- $\alpha$  propionate-1-malonate (INGOLD, PERREN, and THORPE), 1758.

## 26 IV

- $C_{26}H_{19}O_2N_2Br_2$  Acetyl derivative of alizarindipyridinium dibromide (BARNETT and COOK), 1387.  
 $C_{26}H_{21}ON_2Br$  1:4-Diphenyl-3-*p*-bromophenyl-2-*p*-hydroxyphenyl-1:3-dimethindiazidine (INGOLD and PIGGOTT), 2798.

# $C_{27}$ Group.

- $C_{27}H_{26}O_2$  Diacetoxy-7:7-dimethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 560, 562.  
 $C_{27}H_{28}O_2$  Diphenyldihydroxy-*m*- and -*p*-tolylmethanes (MACKENZIE), 1698.



$C_{27}H_{29}O_{11}$  Pelargonin (CURRY), 319.

$C_{27}H_{40}O_{14}$  Ethyl 2:2:4:4-tetracarboxycyclobutane-3-acetate-1-malonate (INGOLD, PERREN, and THORPE), 1788.

## 27 III

$C_{27}H_{21}N_4Cl$  6'-Methylisoquinoline-red (HARRIS and POPE), 1032.

$C_{27}H_{27}O_4N$  Substance, from *p*-dimethylaminobenzaldehyde and methoxyhydroxy-distyryl ketone (BUCK and HEILBRON), 1099.

$C_{27}H_{45}O_4N$  Cevine, preparation of (MACBETH and ROBINSON), 1574.

## 27 IV

$C_{27}H_{21}O_4N_2Br$  Bromomalonotetrabromophenylamide (WEST), 2200.

$C_{27}H_{21}O_4N_2Cl$  Chloromalonotetrabromophenylamide (WEST), 2200.

$C_{27}H_{21}O_4N_2Br$  Bromomalonotetrabromophenylamide (WEST), 2199.

 $C_{28}$  Group.

$C_{28}H_{14}O_4$  Substance, from 2-hydroxyanthraquinone and dextrose (BRADSHAW and PERKIN), 921.

$C_{28}H_{14}O_4$  2:2'-Dihydroxydianthraquinone (BRADSHAW and PERKIN), 921.

$C_{28}H_{14}O_4$  2:2'-Dihydroxydianthryl (PERKIN and WHATTAM), 290.

$C_{28}H_{18}O_4$  3:3'-Dihydroxydianthrone (PERKIN and WHATTAM), 293.

$C_{28}H_{18}N_4$   $\alpha\alpha'$ -Dicyano 2:3-dibenzyl-1:1'-naphthaquinoxaline (DUTT and SEN), 2665.

$C_{28}H_{22}O_4$  Diacetoxy-7-methyl-7-ethyl- $\alpha$ -dinaphthaxanthenes (SINGH and TUCKER), 564.

$C_{28}H_{22}O_4$  Diacetyl derivative of  $\alpha$ -cresolcamphorein (SINGH, RAI, and LAL), 1426.

$C_{28}H_{24}O_{13}$  Methyl heptamethylamygdalinate (HAWORTH and LEITCH), 1924.

## 28 III

$C_{28}H_{22}N_4Cl$  6'-Ethylisoquinoline-red (HARRIS and POPE), 1032.

$C_{28}H_{24}ON_4$  Substance, from N-ethylcarbazole-3-diazonium chloride and ammonia (MORGAN and READ), 2717.

## 28 IV

$C_{28}H_{14}O_4N_2S$   $\alpha\alpha'$ -Dicyano 2:3-dibenzyl-1:1'-naphthaquinoxaline-7-sulphonic acid (DUTT and SEN), 2665.

$C_{28}H_{18}O_4N_2S$   $\alpha\alpha'$ -Dicyano 10-hydroxy 2:3-dibenzyl-1:1'-naphthaquinoxaline-8-sulphonic acid (DUTT and SEN), 2666.

$C_{28}H_{22}O_4N_2S_2$  Di(toluenesulpho)diphenylethylenediamine (CLEGG and PERKIN), 648.

 $C_{29}$  Group.

$C_{29}H_{20}ON_2$  Quinoxaline derivative of 5,6-diketo-7,7-dimethyl-5,6-dihydro- $\alpha$ -dinaphthaxanthene (SINGH and TUCKER), 560.

## 29 IV

$C_{29}H_{22}O_4N_2I$  Diethoxy 1:1'-diethylcarbocyanine iodides (BRAUNHOLTZ), 171.

 $C_{30}$  Group.

$C_{30}H_{20}O_4$  2:2'-Dimethoxydianthraquinone (BRADSHAW and PERKIN), 920.

$C_{30}H_{22}O_4$  3:3'-Dimethoxydianthrone (PERKIN and WHATTAM), 294.

$C_{30}H_{26}O_{11}$  Tetraacetyl derivative of pyrogallolcamphorein (SINGH, RAI, and LAL), 1428.

30 III

- $C_{24}H_{17}O_4N_4$  Dinitroanilinophenanthranaphthazine (SIRCAR and DUTT), 1949.  
 $C_{26}H_{17}ClBr$  2:7-Dibromonaphthaflavinduline (DUTT), 1952.  
 $C_{24}H_{16}O_4N_4$  4-Nitro-5-anilinophenanthranaphthazine (SIRCAR and DUTT), 1949.  
 $C_{30}H_{20}O_4Se$  Selenium dehydrobisdibenzoylmethane (MORGAN, DREW, and BARKER), 2473.  
 $C_{30}H_{20}O_4Se_2$  Selenium dibenzoylmethane (MORGAN, DREW, and BARKER), 2466.  
 $C_{30}H_{20}O_4Se_3$  cycloTriselenium bisdibenzoylmethane (MORGAN, DREW, and BARKER), 2467.  
 $C_{26}H_{20}N_2Cl$  Aminonaphthaflavindulines (DUTT), 1954.  
 $C_{26}H_{21}N_2Cl$  Diaminonaphthaflavindulines (DUTT), 1954.  
 $aa'$ -Dicyano-*o*-1-phenyl-2:3-dibenzylquinoxalinium chloride (DUTT and SEN), 2668.  
 $C_{26}H_{22}ON_2$  Quinoxaline derivative of 5:6-diketo-7-methyl-7-ethyl-5:6-dihydro-*a*-dinaphthaxanthen (SEN-GUPTA and TUCKER), 563.  
 $C_{28}H_{24}O_4Se$  Selenium bisdibenzoylmethane (MORGAN, DREW, and BARKER), 2464.  
 $C_{32}H_{24}O_4Se_2$  Diselenium bisdibenzoylmethane (MORGAN, DREW, and BARKER), 2467.

30 IV

- $C_{26}H_{17}O_4N_2Cl$  Dinitronaphthaflavindulines (DUTT), 1954.  
 $C_{26}H_{18}O_4N_2Cl$  Nitronaphthaflavindulines (DUTT), 1954.  
 $C_{26}H_{18}O_4N_2Br$  3-Bromonaphthaflavinduline nitrate (DUTT), 1953.  
 $C_{26}H_{19}ON_2Cl$  Hydroxynaphthaflavindulines (DUTT), 1955.  
 $C_{26}H_{19}O_2N_2Cl$  Dihydroxynaphthaflavindulines (DUTT), 1954.

30 V

- $C_{26}H_{16}O_2N_2ClBr_2$  Dibromonitronaphthaflavinduline (DUTT), 1955.  
 $C_{26}H_{16}O_2N_2ClBr$  Bromodinitronaphthaflavinduline (DUTT), 1955.

**C<sub>31</sub> Group.**

- $C_{31}H_{22}O_2$  Dibenzoyloxydi-*o*-styryl ketone (BUCK and HELLEROS), 1097.

31 III

- $C_{31}H_{21}ON_2$  Quinoxaline derivative of 5:6-diketo-7:7-diethyl-5:6-dihydro-*a*-dinaphthaxanthen (SEN-GUPTA and TUCKER), 565.  
 $C_{31}H_{21}N_3P$  Triphenylphosphinebenzophenoneazine, reactions of (BRATSKOLTZ), 301

31 IV

- $C_{31}H_{25}O_{11}NS$  1:2:4:5-Tetra-acetoxybenzenesulphamphthalein (DUTT), 2492.  
 $C_{31}H_{25}O_4N_2Cl$  Dichloromalontetrazobenzylamide (WEST), 2201.  
 $C_{31}H_{25}O_4N_2Cl$  Chloromalontetrazobenzylamide (WEST), 2200.  
 $C_{31}H_{25}O_4N_2Br$  Bromomalontetrazobenzylamide (WEST), 2200.

**C<sub>32</sub> Group.**

- $C_{32}H_{20}O_4$  2:2'-Diacetoxydianthraquinone (BRADSHAW and PERKIN), 220.  
 $C_{32}H_{20}O_4$  2:2'-Diacetoxydianthryl (PERKIN and WHATTAM), 291.  
 $C_{32}H_{20}O_4$  3:3'-Diacetoxydianthrone (PERKIN and WHATTAM), 292.  
 $C_{32}H_{20}O_{16}$  1:2:4:5:7:8-Hexa-acetoxyfluoran (MUCKERT), 548.

$C_{23}H_{24}N_4$   $\alpha\alpha'$ -Dicyano-1-*p*-tolyl-2:3-dibenzyl-6-methylquinoxaline (DUTT and SEN), 2666.

$C_{23}H_{24}O_{12}$  Penta-acetylcapsularin (SAHA and CHOUDHURY), 1045.

## 32 III

$C_{23}H_{20}O_2N$  Cevadine (MACNETH and ROBINSON), 1571.

## 32 IV

$C_{33}H_{20}O_2N_4S_3$  Diphenylbisazodia- $\alpha$ -naphthol trisulphide (WATSON and DUTT), 2419.

$C_{33}H_{20}O_2N_4S_2$  Diphenylbisazohydroxynaphthyl mercaptans (WATSON and DUTT), 2416.

 $C_{33}$  Group.

$C_{33}H_{20}O_4N_4S_2$  Substance, from "saccharin" and *m*-phenylenediamine hydrochloride (DUTT), 2393.

$C_{33}H_{20}O_4N_4S_2$  Substance, from "saccharin" and 4:6-diaminoresorcinol hydrochloride (DUTT), 2394.

$C_{33}H_{20}O_4NS$  Dibenzoyl derivative of phenolsulphamphthalein (DUTT), 2390.

 $C_{34}$  Group.

$C_{34}H_{22}N_4Cl$   $\alpha\alpha'$ -Dicyano-1- $\alpha$ -naphthyl-2:3-dibenzylquinoxalinium chloride (DUTT and SEN), 2666.

$\alpha\alpha'$ -Dicyano-1-phenyl-2:3-dibenzyl-1:4-naphthaquinoxalinium chloride (DUTT and SEN), 2666.

 $C_{36}$  Group.

$C_{36}H_{24}N_4$  2:7-Dianilinophenanthranaphthazine (SIRCAR and DUTT), 1948.

$C_{36}H_{32}O_4$  Dibenzoyl derivative of phenolcamphorcin (KRISHNA), 254.

$C_{36}H_{34}O_{21}$  Acetylacertannin (PERKIN and UYEDA), 69.

## 36 III

$C_{36}H_{20}O_2N_4$  Diphthalyl derivative of 2:4:5:7-tetra-amino-1:8-dihydroxy-fluoran (MCKERRI), 549.

$C_{36}H_{20}O_2N_4$  Nitrodianilinophenanthranaphthazine (SIRCAR and DUTT), 1948.

$C_{36}H_{24}O_2N_4$  3-Anilino-naphthaflavinduline nitrate (DUTT), 1953.

$C_{36}H_{24}N_4Cl$   $\alpha\alpha'$ -Dicyano-6-anilino-1-phenyl-2:3-dibenzylquinoxalinium chloride (DUTT and SEN), 2667.

$C_{36}H_{20}O_2N_4$  Base, and its salts, from oxidation of base,  $C_{16}H_{20}ON_2$  (MANN), 2189.

 $C_{37}$  Group.

$C_{37}H_{26}O_4$  5:9-Dibenzoyloxy-7:7-dimethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 562.

 $C_{38}$  Group.

$C_{38}H_{26}O_4$  5:9-Dibenzoyloxy-7-methyl-7-ethyl- $\alpha$ -dinaphthaxanthen (SEN-GUPTA and TUCKER), 564.

$C_{38}H_{26}O_{20}$  Paullinia tannin (NIERENSTEIN), 23.

## 38 III

$C_{38}H_{24}O_{12}Sn_4$  Pentabenzoyl derivative of methylstannonic acid (LAW-BORNE), 2539.

**C<sub>39</sub> Group.**

$C_{39}H_{32}O_{11}N_1$  *o*-Nitrobenzoylcevadine (MACBETH and ROBINSON), 1574..

**C<sub>41</sub> Group.**

$C_{41}H_{40}O_{14}N_3$  Di(*o*-nitrobenzoyl)cevine (MACBETH and ROBINSON), 1575.

**C<sub>42</sub> Group.**

$C_{42}H_{28}O_4$  2:2'-Dibenzoyloxydianthryl (PERKIN and WHATIAM), 291.

**42 III**

$C_{42}H_{22}N_4Cl$  2:7-Dianilinonaphthaflavinduline (DUTT), 1953.

**C<sub>50</sub> Group.**

$C_{50}H_{30}ON_{12}S_{12}$  Substance, from chloropierin and potassium 2-thiol-5-thio-4-phenyl-4:5-dihydro-1:3:4-thiodiazole (RAY and DAS), 325.

**C<sub>51</sub> Group.**

$C_{51}H_{41}O_{20}$  Methoxy-derivative of paullinia tannin (NIERENSTEIN), 27.

**C<sub>52</sub> Group.**

$C_{52}H_{40}O_4N_2S_2As_1$  Substance, from triphenylarsine-*p*-toluenesulphonylimine and *p*-toluenesulphonamide (MANN and POPE), 1054.

# ERRATA.

## VOL. 115 (TRANS., 1915).

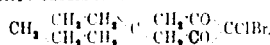
Page Line  
817 2 for "*N*/10-sodium hydroxide" read "*N*/10-sodium hydrosulfide."

## VOL. 117 (TRANS., 1920).

1221 3\* Replace the densities given by—  
" $D_4^{20}$  1.7919,  $D_4^{25}$  1.7701,  $D_4^{30}$  1.7629,  $D_4^{35}$  1.7556,  $D_4^{40}$  1.7484  
Mean coefficient of dilatation between 0° and 30° 0.00083."

## VOL. 119 (TRANS., 1921).

1204 18 for "*dimethylidihydroresorcinol*" read "*cyclohexanespirocyclohexan-3:5-dione*."  
" formula XXXIV should read



1644 12\* and throughout the paper for "*Andropogon ivarowiana*" read "*Andropogon Juvarowiana*."

## VOL. 121 (TRANS., 1922).

35 20 for " $\text{C}_{12}\text{O}_{14}\text{NFe}_4$ " read " $\text{C}_{12}\text{O}_{14}\text{NFe}_6$ ."  
337 21 .. " $\text{Si}_2\text{N}_2\text{Fe}_2$ " read " $\text{Si}_2\text{N}_2\text{Fe}_4$ ."  
575 26 after "on" insert "the reduced."  
600 25 for " $\text{C}_{12}\text{H}_4\text{O}_4\text{Cl}_2\text{Sb}_2$ " read " $\text{C}_{12}\text{H}_4\text{O}_4\text{Cl}_4\text{Sb}_2$ ."  
1134 17\* delete "Baeyer . . . and."  
1304 formula IX should read  $\text{CH}_3\text{CO}-\text{CH}_2\text{CH}(\text{CMeEt})$   
 $\begin{array}{c} + \quad + \\ \text{X}-\text{Br} + \text{Na}-\text{OH}-\text{X.OH} + \text{Na}-\text{Br} \end{array}$   
1394 5 should read " $\text{X}-\text{Br} + \text{Na}-\text{OH}-\text{X.OH} + \text{Na}-\text{Br}$ ."  
1396 bottom for "aqueous" read "alcoholic."  
1642 17 delete "450 grams, or."  
1754 5\* for "solphimines" read "sulphilimines."  
1954 7 .. " $\text{C}_{12}\text{H}_{12}\text{O}_4\text{NCl}$ " read " $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_2\text{Cl}$ ."  
2278 19 .. " $\{\text{N}_1\}$ " read " $\{\text{N}_2\}$ ."  
2411 14\* .. "4½ hours" read "4½ mins."  
2411 16\* .. "61 .." read "61 hours."  
2420 6 .. "A" read " $\frac{\text{A}}{T}$ ."  
2432 6 .. "Part IX" read "Part XI."  
2624 16\* .. "4-nitro" read "4-amino."  
2652 13\* .. " $\text{C}_{14}\text{H}_8\text{O}_4\text{N}_2$ " read " $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_2$ ."

# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 1st, 1922, at 8 p.m.,  
 Professor T. M. LOWRY, C.B.E., F.R.S., Vice-President, in the  
 Chair.

The CHAIRMAN referred to the loss sustained by the Society,  
 through death, of :

	Elected.	Died.
George Robertson Hislop .....	Jan. 29th, 1870.	May 18th, 1922.

The following were formally admitted Fellows of the Chemical  
 Society : A. D. Gay and E. A. Seeley.

Certificates were read for the first time in favour of :

Allin Cottrell, 3, Oxford Terrace, Edinburgh.  
 Reginald William Griffiths, B.Sc., 137, Holly Road, Handsworth, Birmingham.  
 John Watson Jenkin, B.Sc., A.I.C., Tregardock, St. Austell.  
 Ghulam Safdar Khan, B.Sc., Veterinary College, Lahore, India.  
 Hiroshi Nomura, Chemical Institute, Imperial University, Sendai, Japan.  
 Harold Pickles, The Gasworks, Kildwick, Keighley.  
 Stephen John Watson, B.Sc., 35, Oakfield Terrace, Gosforth, Newcastle-on-  
 Tyne.  
 Alexander Mitchell Williams, M.A., D.Sc., Shirley Institute, Didsbury,  
 Manchester.

The following papers were read :

The reactivity of doubly-conjugated unsaturated ketones.

Part III. Unsymmetrical hydroxy- and methoxy-derivatives."

By J. S. BUCK and I. M. HEILBRON.

Phenopyryllium salts of distyryl ketones. Part I." By J. S.  
 BUCK and I. M. HEILBRON.

Ring-chain tautomerism. Part II. The effect of the gem-  
 diethyl group on the carbon tetrahedral angle." By S. S.  
 DESHAFAKDE and J. F. THORPE.

Ordinary Scientific Meeting, held in the Lecture Hall of the Institution of Mechanical Engineers, on Thursday, June 8th, 1922, at 8 p.m., Professor H. E. ARMSTRONG, LL.D., F.R.S., Vice-President, in the Chair.

Dr. H. H. Dale, C.B.E., F.R.S., delivered his Lecture entitled: "Chemical and Physiological Properties." A vote of thanks to the Lecturer, proposed from the Chair, and seconded by Mr. Francis H. Carr, was carried with acclamation, and acknowledged by Dr. Dale.

Ordinary Scientific Meeting, Thursday, June 15th, 1922, at 8 p.m., Sir JAMES WALKER, D.Sc., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of:

	Elected.	Died.
William Gowland .....	Feb. 2nd, 1871.	June 19th.
Thomas Henry Johnson .....	May 5th, 1921.	Feb. 19th.

The following were formally admitted Fellows of the Chemical Society: R. A. Fitzsimons, H. U. Harrow, E. M. James, and H. L. Riley.

Certificates were read for the first time in favour of:

William Leslie Carter, Ellesmere, Bloxidge Street, Langley Green, Birmingham.  
 Wilfred Thomas Grey Davies, B.Sc., Plas y Coed, Derlwyn Road, Tondri, Bridgend.  
 Roy Gardner, B.Sc., Technical High School, Dunedin, New Zealand.  
 John Ernest Jewell, 34, Grove End Road, St. John's Wood, N.W. 8.  
 Charles William Moorhead, 23, Newbridge Road, Bath.  
 Albert Braimah Pearce Page, A.R.C.S., 27, Tanza Road, Hampstead, N.W. 3.  
 Arthur Scholefield, Poulton Hey, Bromborough, Birkenhead.  
 Stanley James Corral Snesker, The Rowans, Wood Hey, Rock Ferry, Birkenhead.

Dr. H. M. Atkinson and Dr. P. C. Austin were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows:

George Baborovsky, Ph.D.	Robert Stanley Colborne, B.Sc.
Stanley John Bailey, B.A.	A.R.C.S.
Harry Baines, B.Sc.	James Brierley Firth, D.Sc., F.I.C.
Frank Belton, B.Sc.	Margaret White Fishenden, D.Sc.
Victor Cecil Branson, B.Sc., A.R.C.S., A.I.C.	Walter Herbert Fulweiler, B.Sc.
Robert Keith Cannon, M.Sc.	Frederick Walter Goldard, M.A.
Bibhu Charan Chatterjee, M.Sc.	Robert Swanson Hall.
	Albert Hassell.

Edmund Langley Hirst, M.A., B.Sc., Ph.D.	Arthur Plowman, B.Sc., A.R.C.S., A.I.C.
Dorothea Annie Hoffert.	John Pryde, B.Sc.
William Job Jenkins.	Juda Hirsch Quastel, B.Sc., A.R.C.S.
Peppo Joseph Levy.	Edmond Samuels.
David McCall, B.Sc.	John Charles Smith, B.Sc.
Richard Edmund Antony Mallet, B.A.	Ronald William Stevenson, M.C., M.A.
Ronald George Wrayford Norrish, B.A.	Valerie Emeline Sophie Swainson, B.Sc.
John Goodrich Oats (Junn.).	Clifford Dane Thomas, B.Sc.
Ralph Henry Parker.	Nowroji Jamsheedji Vazifdar.
Edith Annie Peach.	George William Wigg.
Claude Bernard Meister Platt, M.B.E.	

The following papers were read :

- "Ring-chain tautomerism. Part III. The occurrence of tautomerism of the three-carbon (glutaconic) type between a homocyclic compound and its unsaturated open-chain isomeride." By C. K. INGOLD, E. A. PERREN, and J. F. THORPE.
- "The tautomerism of dyads. Part I. Experiments on the detection of tautomeric equilibria in hydrocyanic acid." By E. H. USHERWOOD.

### LIST OF FELLOWS, 1922.

The List of Fellows for 1922 is being prepared, and changes of address received after July 31st, 1922, cannot be included therein. Fellows whose Christian names and degrees do not appear in full are particularly requested to notify the Assistant Secretary.

Owing to the heavy cost of printing, the List will be sent only to those Fellows who make application prior to August 31st, 1922.

### THE LIBRARY.

The Library will be closed for Stocktaking from Monday, August 7th, until Saturday, August 19th, 1922, inclusive.

During the four weeks August 21st to September 16th the Library will close daily at 5 p.m.

List of Papers received between May 19th and June 15th, 1922 :

- "The interaction of sodium chloride and silica." By F. H. CLEWS and H. V. THOMPSON.
- "Ring-chain tautomerism. Part II. The effect of the gem-diethyl group on the carbon tetrahedral angle." By S. S. DESHAPANDE and J. F. THORPE.



- "Dyes derived from saccharine. The sulphim-phthaleins." By S. DATTA.
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